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for July, 1936

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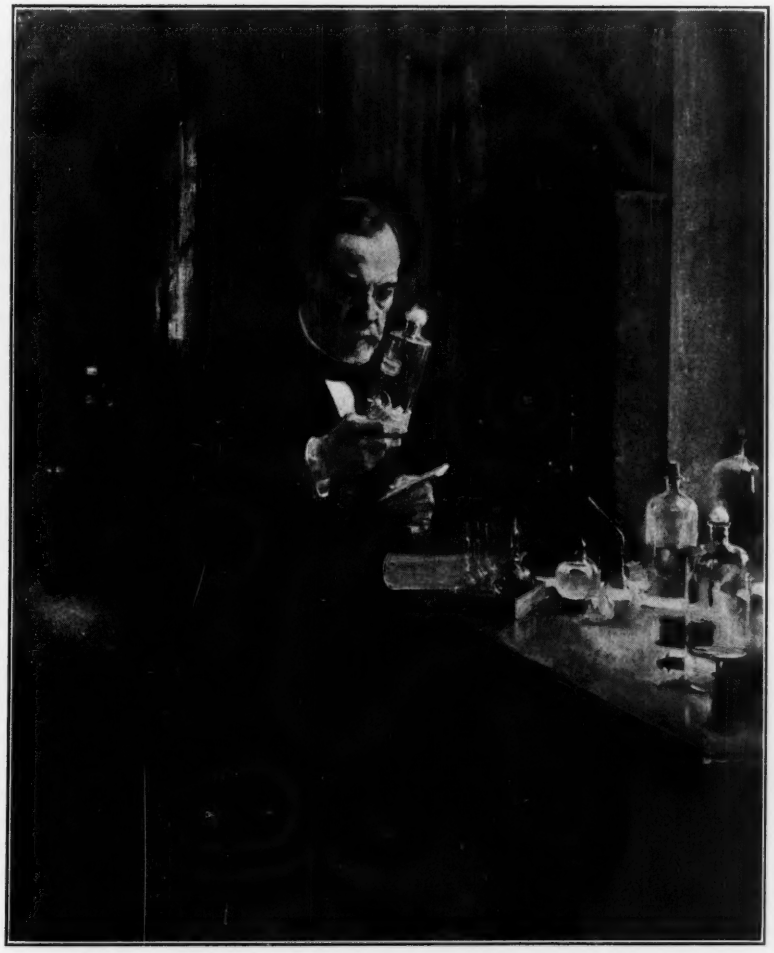

LOUIS PASTEUR (1822–1895)

Pasteur's outstanding contribution to chemistry was his study of optical activity and molecular asymmetry. He is better remembered as the father of the science of bacteriology and the germ theory of disease, and as the inventor of pasteurization.

(*Contributed by Tenney L. Davis.*)

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EDITOR'S OUTLOOK

"EDUCATIONAL ABSTRACTS." The first two numbers (January-February and March-April) of the new bimonthly, *Educational Abstracts*,* lie on our desk. Since the lamented demise of the excellent *Teachers Journal and Abstract*, there has undoubtedly been a need for a publication of this kind, and the new *Abstracts* is evidently undertaking a more ambitious program of coverage of the educational field than has been attempted hitherto.

Abstracts are classified (under 31 topics in the first number and 33 in the second) and are serially numbered. The type is a very legible 8 on 10 (our own abstracts, like *Chemical Abstracts*, are in 8 on 9), set in two 7.5 × 20.0 cm. columns on a 20.0 × 26.5 cm. page. The two numbers now before us are of eighty pages each, and contain a total of 569 abstracts.

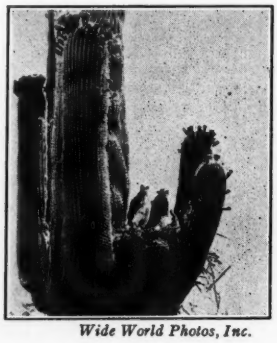
The abstracting is of the digest type, and, although concise, succeeds in avoiding a telegrammatic style. Several abstracts which we checked against the original articles were very good résumés; all appear to be exceptionally well written and edited.

Most science teachers will probably hope that a greater proportion of the space available will eventually be devoted to the "Sciences" section, which has, so far, presented a total of 21 abstracts. Two articles from the January, 1936, JOURNAL OF CHEMICAL EDUCATION have been covered (one in each number); *The American Physics Teacher* and *School Science and Mathematics* have as yet gone unnoticed.

WHERE THE GRASS GROWS GREENEST. A fiction writer in one of the more popular current periodicals has created a heroine whose personality is such, we are told, that, without conscious effort, she charms nearly every man she meets, yet leaves with each the impression that his own perspicacity and sensitivity are the major roots of her attraction for him. In Hollywood she is, like Sylvia, universally adored, but few of her admirers believe that she will be a success on the screen, for few can concede that the general public is capable of perceiving and appreciating the qualities that they themselves discover in her.

If it were still the fashion to construct fiction in the form of allegory rather than for its own sake, our author might well have named his heroine Chemistry. Almost any discussion of reasons why students do or do not "elect" chemistry gives point to this observation. Every chemistry teacher worthy of the name regards the subject as fascinating, but nearly all can think of reasons why it might not place first in a competition for the interests of the average elementary student. It is easy for most of us to see in the biological sciences or in physics superficial charms well calculated to lure the inexperienced student away from our own cherished but less Circean science.

And yet, on second thought, our author might equally well have given his heroine another name. Recently, we were first faintly surprised and then amused to read that at least one physics teacher believes that the biological sciences and chemistry lure away potential students of physics. The reasons given were almost precisely those that a chemistry teacher might have advanced if rôles and names were interchanged. One rather original point, however, both interested and puzzled us. Apparently there is an impression among students that almost anything can, and frequently does, happen in a chemistry laboratory. We wish the physics teacher had either made this point less ambiguously, or had developed and illustrated it more fully. We have missed something somehow, but whether in our own laboratory life or in the physics teacher's argument we cannot decide.



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The cover photograph of a pair of young nesting hawks in the fork of a giant cactus (Carnegiea gigantea) gives some idea of the proportions, the habit of growth, and the flower of this interesting plant.

* Editorial and Business Office: 230 Fifth Avenue, New York City.

The NEUTRON

HUGH A. SHADDUCK

6027 Kimbark Avenue, Chicago, Illinois

A NEUTRON is a nuclear particle with an atomic weight of about one and an atomic number of zero. According to Curie and Joliot (*1*), Nernst was the first to use the word "neutron", but his definition was not the same as the one just given (*2*). The present definition is apparently due to Rutherford (*3*).

In 1920, Harkins (*4*, *5*) at The University of Chicago and Rutherford (*6*) at Cambridge, England, independently suggested that neutrons might possibly exist. A search was conducted at Cambridge for experimental evidence to support this hypothesis, but the results were negative (*3*). It was not until 1930 that a clue was found, and then by an experiment along quite a different line, by workers in another laboratory.

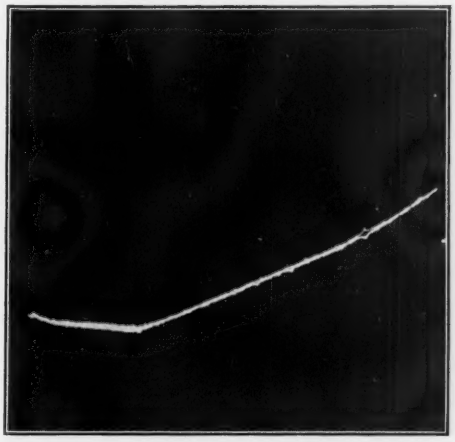
In that year Bothe and Becker, in Germany, reported the discovery of a very penetrating radiation produced by bombarding metallic beryllium with alpha particles from polonium (*7*). Irène Curie, the daughter of Madame Curie, and her husband F. Joliot immediately investigated and confirmed the existence of the very penetrating radiation (*8*, *9*). Tests with an electrometer showed that 4.7 cm. of lead was required to decrease the intensity of the radiation one-half. Curie and Joliot also made the very important discovery that the radiation would eject protons from substances containing hydrogen, such as paraffin (*10*). If the radiation was assumed to consist of gamma rays, calculations indicated that the energy of the photons from beryllium would be of the order of fifty million electron volts (*10*).

Chadwick, at Cambridge, examined the properties of the radiation by means of the valve counter and also an expansion chamber. He observed that the radiation ejected recoil atoms from hydrogen, nitrogen, argon, and other substances. The nitrogen recoil atoms produced more ions and had longer ranges than would be expected if they were propelled by a Compton impact with a photon of the above energy. He writes, "These results, and others I have obtained in the course of the work, are very difficult to explain on the assumption that the radiation from beryllium is a quantum radiation, if energy and momentum are to be conserved in the collisions. The difficulties disappear, however, if it be assumed that the radiation consists of particles of mass one and charge zero, or neutrons" (*11*).

EXPERIMENTAL PROOFS OF THE EXISTENCE OF THE NEUTRON

This brilliant hypothesis was accepted at once by workers in nuclear physics. The group in Paris showed that hydrogen gas and solid paraffin bombarded by the radiation would produce proton tracks in a Wilson cloud chamber (*12*, *13*). They also found that the radiation itself left no track (*13*). This is just what one would expect, for an electrically neutral particle would not attract or repel exterior electrons from atoms or molecules through which it passed. Hence it would not leave a column of electrically charged particles in its path, and there would be no particles on which water droplets could condense to form a track in the Wilson chamber, when the piston was suddenly released.

Doctors Feather (*14*) and Dee (*15*) in England soon published photographs and data that confirmed these results. The existence of the neutron had been established—early in 1932.



Courtesy, Dr. W. D. Harkins and Dr. D. M. Gans

THE DISINTEGRATION OF NITROGEN BY CAPTURE OF THE NEUTRON

The neutron entered from the bottom of the picture as shown in this view.

In addition, Curie and Joliot showed that boron and beryllium when bombarded by alpha rays also gave off gamma rays (*16*). This checked the original observations of Bothe and Becker. However, the absorption of neutrons by various gases and films of various substances differed from that of gamma rays (*1*).

THE MASS OF THE NEUTRON

Chadwick noted that neutrons could be produced from boron as well as from beryllium by bombardment with alpha particles from polonium. The most reasonable equation for the reaction would be:

$$B + He \longrightarrow N + n$$

Assuming conservation of energy and expressing all

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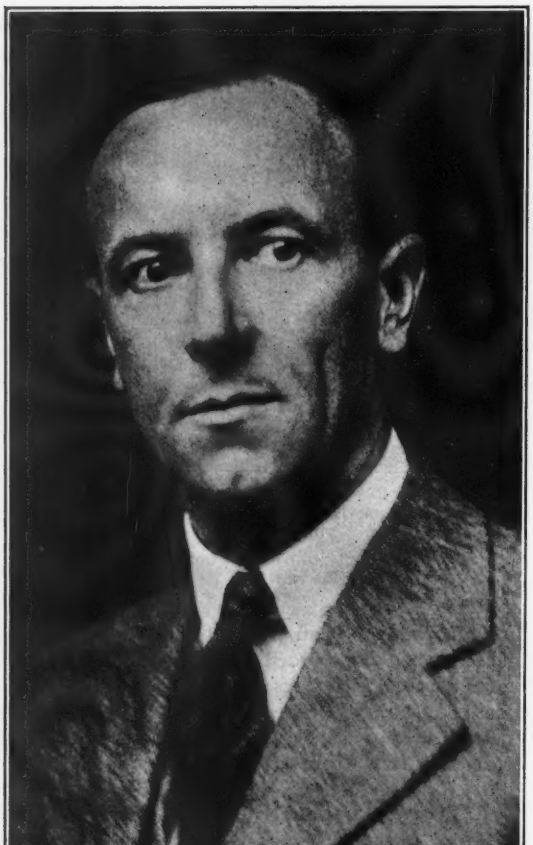
figures in mass units, we have, according to Chadwick (*17*), mass of boron nucleus plus mass of alpha particle plus kinetic energy of alpha particle equals mass of nitrogen nucleus plus mass of neutron plus kinetic energy of nitrogen nucleus plus kinetic energy of neutron, or:

$$11.0083 + 4.0011 + 0.0056 = 14.0042 + x + 0.0006 + 0.0035$$
$$x = 1.0067$$

Recently, discrepancies were noted between the values of the nuclear masses obtained by means of the mass spectrograph, and calculated from the data of atomic disintegrations (*18*, *19*, *20*). The whole subject is now under critical review.

At present, the value for the mass of the neutron given by Chadwick and Goldhaber (*21*, *22*) is accepted tentatively. They studied the disintegration of heavy hydrogen by hard gamma rays from thorium C″, and established the reaction



Courtesy, Scientific Monthly

PROFESSOR JAMES CHADWICK

Professor Chadwick, one of the most able and fruitful workers in the Cavendish Laboratory for fully twenty years, has recently left that post to accept the professorship of physics in the University of Liverpool. His name has been associated with many important problems in the field of radioactivity and atomic physics.

$$D^2 + h\nu \longrightarrow H^1 + n^1$$

From disintegration data, the mass of the deuteron is 2.0142, and the mass of the proton is 1.0081 (*19*). The gamma rays had an energy of 2.62×10^6 electron volts, equivalent to 0.0029 mass unit; the kinetic energy of the proton and the neutron equaled 0.0006 mass unit. Then the mass of the neutron is found from the equation

$$n = (2.0142 + 0.0029) - (1.0081 + 0.0006)$$
$$n = 1.0084$$

THE CHARGE ON THE NEUTRON

The great penetrating power of the stream of particles from (beryllium plus polonium) agreed with the assumption of their neutral character. The Wilson cloud track photographs confirmed it. Calculations by Dee indicated that the ionization along the path of the neutron was less than one ion-pair per three meters of air (*15*).

NEUTRON VOLUME AND DENSITY

Since the neutron lacks exterior electrons, its volume is approximately that of a hydrogen nucleus. The radius of a hydrogen nucleus or proton is about 10^{-13} cm. The radius of a hydrogen atom is about 10^{-8} cm. Harkins points out that a million million neutrons could be contained in the volume of an ordinary atom and still leave room to spare (*23*). The density of the neutron is correspondingly high (*23*).

THE NATURE OF THE NEUTRON

Several suggestions as to the nature of the neutron have been advanced. According to Chadwick the neutron may be a proton imbedded in an electron, something like a condensed hydrogen atom, with a binding energy of about one million electron volts (*17*). Such a unit would possess a zero electrical charge at a short distance, since the positive charge of the proton would be neutralized by the negative charge of the electron.

Schüler and Schmidt suggest that it may consist partly of particles composed of a negative proton and a positron (*24*). The positron is the positive counterpart of the negative electron.

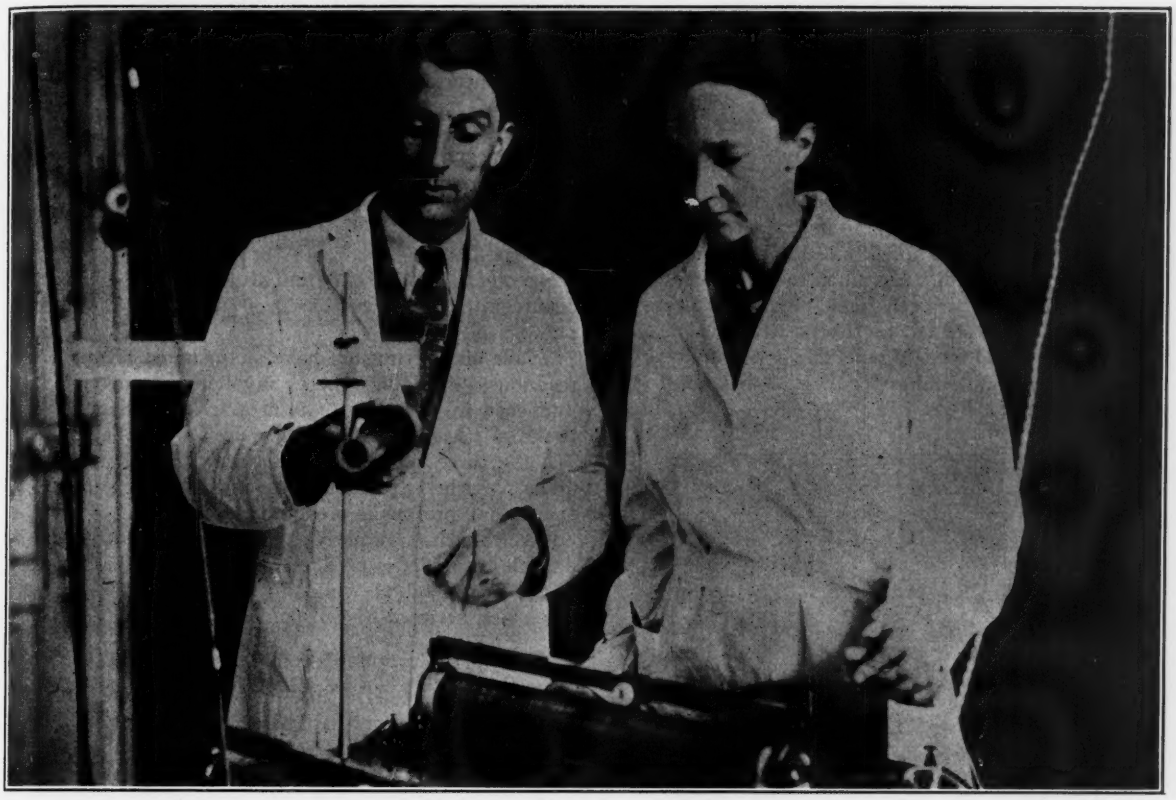
According to Longinescu, the neutron is a fundamental entity—the unit of mass itself (*25*). On this basis, a proton is a combination of a neutron and a positron.

As yet the data are insufficient to warrant a decision in favor of any of these views. Most investigators have adopted the proton-electron picture.

CHEMICAL PROPERTIES OF THE NEUTRON

From the standpoint of chemistry, the neutron represents a particle of zero nuclear charge and, therefore, of zero atomic number. The discovery of the neutron and the data of the periodic table show that one chemical element exists for every positive integer from zero to ninety-two, both inclusive.

Dr. Harkins has suggested the name "neuton" for



Courtesy, Scientific Monthly

FRÉDÉRIC JOLIOT AND IRÈNE JOLIOT CURIE

the element of zero atomic number—the element consisting of neutrons (*26*). Since the neutron has no exterior electrons it cannot form chemical compounds but it can react with atomic nuclei to form other elements.

THE PRODUCTION OF NEUTRONS

Neutrons may be produced from a number of elements (as such or in suitable compounds) by bombarding them with alpha particles from radioactive substances (*27*). Beryllium, however, appears to give the best yields (*8, 9*). A little metallic beryllium in granular form may be mixed with a small quantity of radioactive material, often obtained by the chemical treatment of used radon tubes from hospitals. The mixture is placed in a suitable container and then set into the apparatus chosen for the experiment. This serves as a source of neutrons as long as the alpha rays are sufficiently intense. For cloud tracks, the source is often placed in a hole in the center of the glass plate forming the top of the chamber (*14*). The source may also be placed outside the Wilson chamber (*13*). When an ionization chamber is used, the neutrons may be produced by the impact of alpha rays on a small disk of beryllium (*17*). The equation for the nuclear reaction may be written* (*11*):

$$ {}_4Be^9 + {}_2He^4 \longrightarrow {}_6C^{13} \longrightarrow {}_6C^{12} + {}_0n^1 $$

Neutrons have also been produced from lithium (*28*), boron (*10, 29*), fluorine (as fluorite) (*27, 30*), aluminum (*13, 27, 31*), and sodium (*32*). According to recent experiments in California neutrons can be produced by bombarding beryllium with helium ions artificially speeded up to energies of a million volts (*33*).

High speed deuterons will produce neutrons from lithium chloride and beryllium with yields several hundred times those obtained by accelerated helium ions, as indicated by a sensitive electroscope coated inside with paraffin, and about "100 times the intensity obtained by the strongest polonium source now in use" (*34*). Deuterons will also produce neutrons from targets of compounds containing deuterium, such as "heavy" phosphoric acid, sodium deuteroxide, etc. (*20, 35, 36, 37*):

$$ {}_1H^2 + {}_1H^2 \longrightarrow {}_2He^3 + {}_0n^1 $$
$$ {}_4Be^9 + {}_1H^2 \longrightarrow {}_5B^{10} + {}_0n^1 $$

Even hard gamma rays can produce neutrons from "heavy" water (*22*) and from beryllium (*38, 22*).

* In the equation the superscript refers to the mass number of the atom, the subscript to the atomic number.

COLLISIONS AND DISINTEGRATIONS

When neutrons pass through matter containing hydrogen, protons are ejected. Thus, when a Wilson chamber filled with hydrogen gas was subjected to neutron bombardment, proton tracks were observed. These tracks were also produced when the neutrons passed through a paraffined surface.

When nitrogen gas in a Wilson chamber was bombarded by neutrons, photographs showed that atomic disintegration occurred (*14, 39*). Although these events are relatively rare they are much more frequent than disintegrations of nitrogen nuclei by alpha particles. This might be expected, as the positive field around the nucleus would tend to repel the positively charged alpha particle, but would offer little obstruction to the neutral neutron.

WILLIAM D. HARKINS

MacLeish Distinguished Service Professor of Chemistry at The University of Chicago. He has made notable contributions to the subject of atomic nuclei. At present, he and his associates are actively engaged in a study of the neutron.

When such disintegrations occurred, the appearance of the Wilson photographs indicated that an alpha particle rather than a proton was ejected from the nucleus hit by the neutron. This has been confirmed by a mathematical analysis of the V-shaped track produced (*14*). The incoming neutron leaves no track. The equation for the reaction may be written:

$$_7N^{14} + {}_0n^1 \longrightarrow {}_7N^{15} \longrightarrow {}_5B^{11} + {}_2He^4$$

Harkins and Gans have shown that in a disintegration the neutron is captured by the nitrogen nucleus (*40*), a possibility first noted by Dr. Feather (*14*).

It was stated above that when boron was bombarded by alpha rays, neutrons were produced, thus:

$$_5B^{11} + {}_2He^4 \longrightarrow {}_7N^{15} \longrightarrow {}_7N^{14} + {}_0n^1$$

This appears to be a reversible nuclear reaction, for which there may be an equilibrium condition. We may write (*14, 41, 42*)

$$_7N^{14} + {}_0n^1 \rightleftharpoons {}_5B^{11} + {}_2He^4$$

Oxygen (*43*), fluorine (*44*), and neon (*45*) have also been disintegrated by neutrons, as shown by Wilson photographs.

Evans and Livingston have summarized all nuclear reactions, including those involving neutrons, as published up to May, 1935, in a series of charts and tables in *Reviews of Modern Physics* (*46*). They state, "Of the three types of neutron reactions, that giving alpha particles is predominant for very light elements; that giving protons is predominant around $Z = 10$ to 30; the third, or radiative type, in which there is no particle emission, is predominant in the higher ranges of the atomic table; while all three processes occur in the region between $Z = 20$ and 30."

INDUCED RADIOACTIVITY

In January, 1934, Curie and Joliot reported the remarkable discovery that boron, magnesium, and aluminum become radioactive after bombardment with alpha particles (*47*). Boron, for instance, emits positrons for some time after the source of alpha rays is removed. The half-life for the irradiated boron was fourteen minutes, for magnesium two-and-a-half minutes, and for aluminum three minutes and fifteen seconds. They suggested that this activity is due to the formation of radio-nitrogen, $_7N^{13}$, radio-silicon, $_{14}Si^{27}$, and radio-phosphorus $_{15}P^{30}$ from $_5B^{10}$, $_{12}Mg^{24}$, and $_{13}Al^{27}$, respectively. The equation for boron would be:

$$_5B^{10} + {}_2He^4 \longrightarrow {}_7N^{13} + {}_0n^1$$
$$_7N^{13} \longrightarrow {}_6C^{13} + e^+$$

This was confirmed by chemical tests, which showed that ammonia formed from boron nitride was radioactive. The irradiated aluminum was tested by treating with hydrochloric acid. The activity followed the gas evolved, which would correspond to the formation of phosphine (*48, 49*).

Enrico Fermi and his associates, in Italy, followed this lead and showed that over forty elements could be made radioactive, this time by bombardment with neutrons (*50, 51*). The half-lives varied from a few seconds to a day or more. He proved the presence of an element different from the original irradiated element by means of the isotopic method of analysis. Thus irradiated phosphorus produced a very small amount of radio-silicon, $_{14}Si^{31}$, which emitted negative electrons. The original articles give in considerable detail the results of the irradiations and of the chemical and other tests applied to each of the substances studied.

The half-lives of the activated elements are being determined with some care, as these values give useful information about active elements produced in nuclear reactions (*52*, *53*).

It is interesting to note that radioactive $_{13}Al^{28}$ can be formed in five distinct ways (*54*).

$$_{13}Al^{27} + {}_0n^1 \longrightarrow {}_{13}Al^{28}$$
$$_{14}Si^{28} + {}_0n^1 \longrightarrow {}_{13}Al^{28} + {}_1H^1$$
$$_{15}P^{31} + {}_0n^1 \longrightarrow {}_{13}Al^{28} + {}_2He^4$$
$$_{13}Al^{27} + {}_1D^2 \longrightarrow {}_{13}Al^{28} + {}_1H^1$$
$$_{12}Mg^{25} + {}_2He^4 \longrightarrow {}_{13}Al^{28} + {}_1H^1$$

In each case the aluminum gives off a negative electron to form stable silicon. The half-life of the active aluminum is 156 ± 5 seconds (*64*).

$$_{13}Al^{28} \longrightarrow {}_{14}Si^{28} + e^-$$

Fermi has suggested that elements 93 and 94 may be formed by bombarding uranium with neutrons (*55*). A number of investigators are now checking this observation.

SLOW NEUTRONS

"In our previous work," writes Fermi and his staff (*51*), "we had noticed some irregularities in the intensity of activation of silver by neutrons from a radon-beryllium source, which apparently depended on some not very clear geometrical factors. Further investigation showed that the activation was strongly influenced by objects surrounding the neutron source, and in particular that the activation could be enormously increased by surrounding the source and the activated substance with a large amount of water or paraffin wax. The effect appeared at once to be due to the presence of hydrogen, as other substances not containing hydrogen failed to give comparable effects." Some substances, *e. g.*, sodium and silver, showed an increased activity when irradiated under water; others, *e. g.*, silicon and magnesium, were not affected (*51*).

It appeared that the fast neutrons from the source were slowed down by elastic collisions with the hydrogen in the water or paraffin and that these slower neutrons were much more readily captured by the nuclei of certain elements. It was found that the capture cross-section for a neutron-nucleus combination ranged widely, from values about the same as for fast neutrons to values many times larger. Cadmium in particular gave a capture cross-section of $10{,}000 \times 10^{-24}$ cm.^{2} (*51*).

These results were subjected to a check at once by a number of researchers, among them Dunning and his co-workers (*56*) at Columbia University. They studied the effects of slow neutrons on a large number of elements and found neutron-nucleus cross-sections that varied from 3.5×10^{-24} cm.^{2} for deuterium and 1.4×10^{-24} cm.^{2} for sulfur to $30{,}000 \times 10^{-24}$ cm.^{2} for gadolinium, while for fast neutrons (of the order of 1 m.e.v. energy) the capture cross-section for deuterium was 1.68×10^{-24} cm.^{2} and for sulfur 2.6×10^{-24} cm.^{2} During their work they devised an ingenious velocity selector for neutrons (*57*).

The cross-section for a neutron capture by a particular nucleus appears to be a function both of the energy of the neutron and the nature of the nucleus (*56*, *58*, *59*, *60*, *61*). According to Moon and Tilman (*60*), "a considerable proportion of the neutrons traversing the wax and effective in producing radioactivity in silver had velocities at least comparable with those of thermal agitation."

CONCLUSION

Workers in many laboratories are studying the production and properties of neutrons. The energy balance in neutron reactions is of great interest at present, Methods of producing high-speed nuclei artificially are receiving widespread attention. Of the several ways now known, the best at present appears to be that devised by Lawrence and his co-workers at the University of California, and recently described by Livingston (*62*). By means of this apparatus, called a "cyclotron," it is possible to produce a beam of deuterons with an energy equivalent to about six million electron volts (*63*).

The discovery of the neutron and of induced radioactivity are without doubt among the most important in the physical sciences in recent years. The Nobel prize in physics for 1935 was presented to Professor Chadwick for his discovery of the neutron; the Nobel prize in chemistry for 1935 to Irène Joliot Curie and Frédéric Joliot, jointly, for their discovery of induced radioactivity.

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At the Pittsburgh meeting of the Division of Chemical Education of the American Chemical Society, September 7–11, there will be a general round table discussion of the teaching of the modern theory of electrolytes and conceptions of acids, bases, and salts. It is hoped that a number of the most active and progressive teachers of chemistry will be present and contribute their personal experiences in this matter. It is a question of very live interest, and many teachers will welcome the opportunity to learn how to bring their courses strictly up to date.

The COMPOSITION *and* USES *of the* FRUIT *of the* GIANT CACTUS (*CARNEGIEA GIGANTEA*) *and* ITS PRODUCTS

ROBERT A. GREENE

Department of Agricultural Chemistry, University of Arizona, Tucson, Arizona

INTRODUCTION

THE living conditions of primitive peoples depend upon two factors: (1) the materials available for food, shelter, and clothing; and (2) the intelligence and resourcefulness of the individual. Where there is an abundance of available materials, the native may maintain a satisfactory standard of living at a minimum of mental and physical effort; where there is a shortage of materials, the native must exert himself or else his existence will terminate.

In arid regions where the annual rainfall is small, and where there are no streams that may be used for irrigation, the natives are forced to use the plants occurring in abundance around them. The cacti are probably the most abundant and are certainly the most characteristic and picturesque of our desert plants. Because of this, it is only natural that resident peoples should turn to them as sources of food.

The Sahuaro, or "giant cactus" (*Carnegiea gigantea*), is the largest and one of the most common of the cacti in Southern Arizona and Northern Sonora, Mexico. In this region, which is the home of the Papago and Pima Indians, the Sahuaro is abundant and is used by these tribes as a source of food.

Thackery and Leding (*4*) have given an interesting, illustrated account of the fruits of various cacti, as well as their uses and the products prepared by the Indians.

During the past few years the author has analyzed a number of the products of the Sahuaro and from these analyses the data presented were secured.

HARVESTING THE FRUIT

The fruit of the Sahuaro ripens, according to locality, during June and July, and is harvested by the Indians at that time—usually until the summer rains commence. At harvest time the Indians migrate to the Sahuaro forests and establish harvest camps. The fruit is removed from the Sahuaro by means of a pole which is constructed from the rib of a dead Sahuaro. A fork of creosote bush or Catclaw is tied on so as to form a hook, and by means of this pole the fruit may be dislodged. The fruit is then picked up, and as it is gathered the outer husks (if not broken during the dislodging process) are split by means of the thumbnail, and the contents (pulp) placed in a basket. Thackery and Leding (*4*) give the following description:

"Upon returning to camp with the basket full of pulp, it is placed in a large olla or earthen jar of native manufacture. A small quantity of water is added and the cooking begun. After cooking for half an hour the juice is well separated from the seeds and pulp, and it is then strained into another olla. Ordinary screen wire is used as a strainer, and being rather coarse for the purpose it permits a portion of the seed and pulp to pass through with the sirup. In the old days the Papagos made a strainer by weaving together the long leaves of the Sotol plant (*Dasylirion wheeleri*) and doubtless it served the purpose better than its modern substitute. . . . After the cooked pulp has been thoroughly drained, the juice is returned to the fire and is allowed to cook slowly for about an hour, by which time it has become quite sirupy and is then ready for consumption or storage. A small amount of preserves is sometimes made, this being merely the unstrained pulp cooked to the desired consistency. . . . The portion to be kept for future use is placed in ollas and sealed tight, the seal being accomplished with a piece of broken pottery chipped into circular form to fit the mouth of the olla. This crudely constructed cover is held in place either by a preparation of adobe mixed with fine grass, or a transparent, yellowish brown gum or lac gathered from the 'Samo prieto' (*Coursetia glandulosa*), upon which it is produced by a scale insect (*Tachardiella fulgens*). When properly put up in this manner the sirup or preserve will keep more than a year."

The sirup is a deep reddish brown in color and in appearance and in taste is not greatly unlike sorghum molasses, although it usually has a somewhat burnt taste.

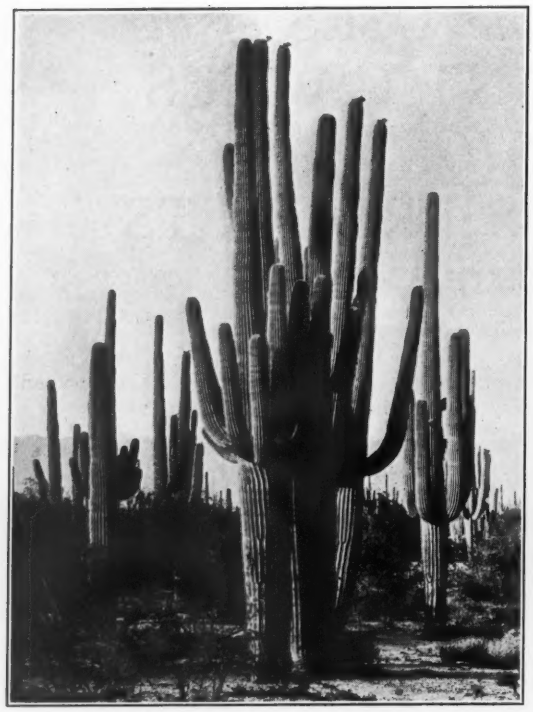
Sometimes the pulp is not made into sirup, but is dried in the sun and may be eaten dry. According to Thackery and Leding (*4*), sirup may sometimes be made from the dried pulp.

The seeds and fiber strained out in the preparation of the sirup are also dried in the sun and at present are used chiefly for chicken feed. In the past, the seeds were consumed by the Indians. However, there is an extremely hard seed coat which may have interfered with its use as human food. This is probably responsible for certain depraved habits of a few tribes. W. J. McGee in his monograph on the Seri Indians (*3*) says:

"All of the cacti of the region* yield Tunas† in considerable quantity . . . ; the huge saguaro affords an enormous annual yield . . . . The fruits are eaten in enormous quantity and are

* Seriland: Tiburton Island and the adjoining Sonoran Mainland.

† A common name for the fruits of cacti.



Courtesy R. B. Streets

Courtesy W. E. Bryan

TWO VIEWS OF THE GIANT CACTUS IN ITS NATURAL SETTING

imperfectly digested, the hard, coated seeds especially passing through the system unchanged; the feces containing these seeds are preserved with some care and after the harvest is passed the hoard (desiccated, of course, in the dry climate) is ground between hupf and ahst,* and winnowed in baskets precisely as are the mesquite beans; and the product is then eaten either dry or in the form of atole like the mesquite meal. . . . this . . . is the 'second harvest' of the California Indians as described by Clavigero, Baegert and others."

The products of the fruits of the Sahuaro are: (1) the sugary pulp from which (2) the sirup is prepared; (3) the "rag" or the residue remaining after the extraction of sugars and separation of seeds; (4) the seeds. In addition to the sirup and the preserve (which are prepared by boiling the unstrained pulp to the desired consistency) a wine, which will be discussed later, is prepared from the sirup.

ANALYTICAL DATA

Samples of the fruit, pulp, rag, sirup, preserve, seeds, and wine were secured from the Papago Indians, and were analyzed according to the methods of the Association of Official Agricultural Chemists (*1*). The composition of the sirup and preserve is set forth in Table 1.

TABLE 1

	Sirup	*Preserve*
Total Solids	67.73%	69.00%
Reducing Sugars (as dextrose)	62.52	61.28
Protein	3.36	3.22
Ash	1.04	1.19
Acid (as malic)	0.64	0.69
	67.56	66.38
Difference (pigments, non-reducing sugars, etc.)	0.17	2.62
	67.73%	69.00%

* A primitive grinding mill.

Further examination showed that inversion did not increase the quantity of reducing sugars. It seems likely that during the period of boiling, the simpler polysaccharides, if present originally, would be hydrolyzed.

A proximate analysis as usually applied to feeding materials was made and the results are recorded in Table 2 (air-dry basis):

TABLE 2

	Whole Fruit	*Pulp*	*Rag*	*Seeds*
Moisture	3.75%	1.60%	19.15%	6.46%
Ash	6.91	3.23	4.80	2.34
Protein	13.06	14.62	11.19	15.75
Ether Extract	9.93	20.05	3.62	21.44
Crude Fiber	13.35	25.96	5.30	28.44
Nitrogen-free Extract	53.00	34.54	55.94	25.57

The results given above were made upon air-dry samples. When the materials were received, a moisture determination was made, and the results calculated on the weight of the fresh material were: pulp, 40.07%; whole fruit, 82.50%.

Sugar determinations were made upon a new series of these materials, all of them showing the presence of considerable amounts of sugar. It seems likely that in the preparation of the sirup, the seeds become impregnated with sugar. In the case of the rag, there is a considerable amount of residual sugar, due to incomplete extraction. The distribution of reducing

sugars (as dextrose) in these materials before and after inversion with invertase is shown in Table 3 (sugars expressed on the basis of air-dry material).

TABLE 3

	Before Inversion	*After Inversion*
Whole Fruit	3.5%	6.6%
Pulp	7.1	9.9
Rag	15.9	19.3
Seeds	6.4	8.9

These results are somewhat misleading. The sugar is found in the pulp, but when the results are expressed as percentages, the weight of the seeds present lowers the percentage of sugar. The same is true of the whole fruit. The high sugar content of the "rag" can be explained on the basis of incomplete extraction and concentration due to desiccation. The results show that the seeds apparently contain some reducing sugars, but it seems probable that these results were secured because the seeds had become impregnated with sugar. Table 3 shows that while reducing sugars are chiefly found, there do occur some simple polysaccharides which are hydrolyzed by acids or invertase. Qualitative tests indicated that dextrose was probably the sugar found in largest amounts and that the disaccharide was probably sucrose. The seeds were examined for starch by means of the iodine test, which gave positive results.

The sirup, preserve, and fruit were tested for pectin, which was not found to be present. This will explain the difficulty which has been encountered in preparing jellies from cactus fruits. Many housewives have attempted this, particularly with the fruit of the prickly pear, but the results have usually been disappointing. The author has seen a few samples of jellies and jams, said to have been prepared from the fruits of various cacti.

The chemical composition of the sirup is not greatly unlike other sugar concentrates. According to Leach (*2*), molasses may contain 14 to 20 per cent. sucrose and 30 to 33 per cent. dextrose; maple sirup, 40 to 51 per cent. sucrose and 10 to 17 per cent. dextrose. Jellies usually contain 45 to 80 per cent. solids (15 to 75 per cent. sugar). The sirup from the fruit of the cactus, however, consists chiefly of reducing sugars. Most plants serving as commercial sources of sugar (maple sap, sugar beet, sugar cane) contain sucrose as the principal sugar; many other plants, particularly fruits (cherries, figs, grapes, pears, gooseberries) contain reducing sugars (chiefly dextrose) and only small amounts of sucrose. Honey also consists of a large percentage of invert sugar and traces of sucrose.

The whole fruit contains approximately 6.6 per cent. sugar (after inversion) on the air-dry basis. The sugar is concentrated in the fibrous material surrounding the seeds. By way of comparison it might be mentioned that the sugar beet contains an average amount of approximately 14.4 per cent. sucrose; sugar-cane juice, 12 to 20 per cent. sucrose; maple sap, 0.7 to 2.78 per cent. sucrose; the juice of the sorghum plant (*Andropogon sorghum var. saccharatus*) contains 2.8 to 8.0 per cent. sucrose and 3.8 to 7.5 per cent. reducing sugar. So the fruit of the cactus compares favorably with common sources of sugar.

"TISWIN"—CACTUS WINE

All the sirup, however, does not go into the manufacture of jam. Each year (usually in August, shortly after the harvest, when temperatures are favorable for fermentation) a certain part is diverted into the preparation of an alcoholic beverage, which is called "tiswin." The significance of the wine-making and the harvest season may be understood from the following quotation from Thackery and Leding (*4*):

> "The importance of this fruit to these people in olden times is indicated by the fact that they began their calendar year at the harvest time, a custom which still persists. The fiesta to celebrate this event is known to them as 'Navaita,' a Papago word derived from 'Navait,'* meaning wine, and suggested by the wine-making from the fruit of the cactus. It is evident, from information procured from the older Papago Indians of today, that in former times the intoxicating drink which was made from the juice of the fruits of the Sahuaro was very generally used in the religious supplications for rain, in the firm conviction that without it rain would fail to come."

A sample of tiswin was secured from an old Papago familiar with its manufacture. According to the wine-maker, tiswin is prepared by diluting one part of the sirup with four parts of water. The mixture is placed in an olla and allowed to ferment. (The fermenting organisms either occur in the sirup or come from the air.) The usual time of fermentation is approximately 60 hours. At this time, fermentation is not complete, so the wine contains a considerable quantity of carbon dioxide and unfermented sugar.

The wine had a ruby-red color, but was somewhat turbid. It had a very agreeable odor and taste and was not unlike strawberry wine, which is prepared in certain sections of the country.

An analysis of the wine, according to the methods of the Association of Official Agricultural Chemists (*1*), gave the results recorded in Table 4.

TABLE 4

Specific Gravity	1.0284
Alcohol	4.9% (volume)
	3.9% (weight)
	3.87 grams/100 cc.
Glycerol	0.568%
Total Acids (as tartaric)	0.739
Volatile Acids (as acetic)	0.194
Reducing Sugars (as invert)	7.0
Protein	0.615
Ash	0.368
Extract	9.84
Acid-insoluble Ash	0.09
Alkalinity of Ash	2.84 cc. of *N*/10 acid
Alkalinity of Insoluble Ash	0.9 cc. of *N*/10 acid
Glycerol-Alcohol Ratio	13.7:100

The results given in the table were compared with a compilation of analyses of wines given by Leach (*2*). In general, the composition of tiswin is similar to that of port, sherry, or tokay. With the exception of the alcoholic content, which is much lower than that of the wines just mentioned, the glycerol, reducing sugars,

* Navait is the general name for wine. Tiswin is the wine prepared from the cactus.

specific gravity, and total acids occur in approximately the same quantities. The protein and ash values are within the limits of the usual values for port, sherry, and tokay; the glycerol-alcohol ratio is low; and the volatile acids are found in slightly greater amounts than in tokay. It seems probable that if fermentation were allowed to proceed until the alcoholic content was greater, tiswin would not be greatly different from the wines mentioned above.

It has been stated that tiswin was used primarily in connection with religious rites. In certain rare cases it was used to excess, as is shown by the following quotation of Thackery and Leding (*4*) from the "Diary and Itinerary of Francisco Garces" (translated by Elliot Coues). Francisco Garces was a noted Catholic missionary, and he describes a feast celebrating his arrival at a village of the Pima Indians in September, 1776:

"I arrived at the Pima Gilenos, accompanied by the governor of the Cocomaricopas. There was great rejoicement, for there had spread thus far the report that they (the Moquis) had me killed. The governor of the Pimas told me that all of the relatives were well content and wishing to make a feast, all the pueblos together. I agreed to this, but on condition that it should be apart from me, foreseeing in this what would come to pass. In a little while I heard that they were singing 'a heap' (*de monton*); this was stopped presently, but was followed by a great uproar of discordant voices, and shouting, in which they said 'We are good. We are happy. We know God. We are the fellows to fight the Apaches. We are glad the old man (as they call me) has come and not been killed.' This extravagant shouting (*exorbitante griteria*), a thing foreign to the seriousness of the Pimas, I knew came from drinking, which produced various effects. Some came and took me by the hand, saluting me. One said, 'I am Padre de Pedro.' Another said to me, 'Thou hast to baptize a child.' Another, 'This is thy home, betake not thyself to see the king nor to Tucson.' Others made the sign of the cross, partly in Spanish; so that though I felt very angry at such general drunkenness, there did not fail me some gusto to hear the good expressions into which they burst even when deprived of reason. The next day I complained of these excesses to the governor, who told me that it only happened a few times, and in the season of the saguaro, and adding that it made his people vomit yellow and kept them in good health. What most pleased me was to see that no woman got drunk; instead of which I saw many of them leading, by the bridle, the horse upon which her husband was mounted, gathering at the same time the clothes and beads that the men scattered about, in order that none should be lost."

"MA-KUM"

"Ma-kum" was prepared from the caterpillar of the sphinx moth (*Celerio lineata*), which appears after the summer rains have caused the grass to become green. This caterpillar only lives for a short time and is found chiefly in the foothills. The Indians gathered the caterpillars, ground them into dough, spread this out, and allowed it to dry in thin layers in the sun. At the time of the fiesta, the wine (which had been prepared) was placed in a large olla, and the Indians would gather around the olla, drinking the wine and eating ma-kum, and sometimes the catkins from cotton-wood trees. Possibly the Indian was not so primitive after all: he had a sparkling wine, and "cakes" to be munched as the wine was sipped.

This old order has changed. The Papago no longer eats ma-kum as did the "ho-ho-kum" ("ancient ones"). Very few of the older Indians will admit that they have ever eaten ma-kum, yet I know that Cha-Ma-Riah, the old Papago who is technical assistant in our department (one time a student at Haskell Institute, and an employee of the University of Arizona for thirty years) secretly longs for the time when he can retire to his ranch in the shadow of Baboquivari, and when he too may have tiswin and ma-kum as did his ancestors, the ho-ho-kum.

The manufacture of tiswin is interesting, however, because the American Indian tribes, in general, did not manufacture alcoholic beverages. The Indians of the East and Middlewest apparently were introduced to "fire-water" with the coming of the trader. It seems odd that none of those Indians had developed the art of wine-making. There were plenty of berries and fruits which might have been fermented. The Mexican Indians practiced the manufacture of pulque from the sap of the Agave long before the Spaniard conquered Mexico. There is no means of knowing whether the manufacture of tiswin is original with the Papagos and Pimas or whether they learned the art of wine-making from their Mexican cousins. Only a few tribes of the Southwest manufactured wine. Apparently the Navajos and Hopis never brewed any intoxicating drink, but the Apaches have a beverage called "tulapai" which is made from fermented corn, to which they add a liquid obtained by steeping the roots of a shrub which is found abundantly on their reservation. This shrub apparently has a slight narcotic content.

It was suspected that the reason tiswin was consumed before fermentation had ceased was probably due to the fact that acetic fermentation proceeded rapidly. A sample of tiswin which had been stored in an ice box for more than a year was examined and found to contain approximately 5 per cent. of acetic acid.

SUMMARY

Thus, the fruit of the giant cactus supplies the Indian with a variety of edible products: a palatable sirup, not greatly unlike maple sirup or molasses; the dried pulp, from which the sirup may be prepared; the seeds, which may serve as a source of protein; a wine for religious rites; and a vinegar for domestic purposes.

ACKNOWLEDGMENTS

The author gratefully acknowledges the assistance and suggestions of Dr. R. H. Forbes, Tucson, Arizona, who suggested this investigation and who secured the samples for analysis.

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RUSKA'S RESEARCHES *on the* ALCHEMY *of* AL-RAZI*

RUDOLF WINDERLICH

Oldenburg in Oldenburg, Germany

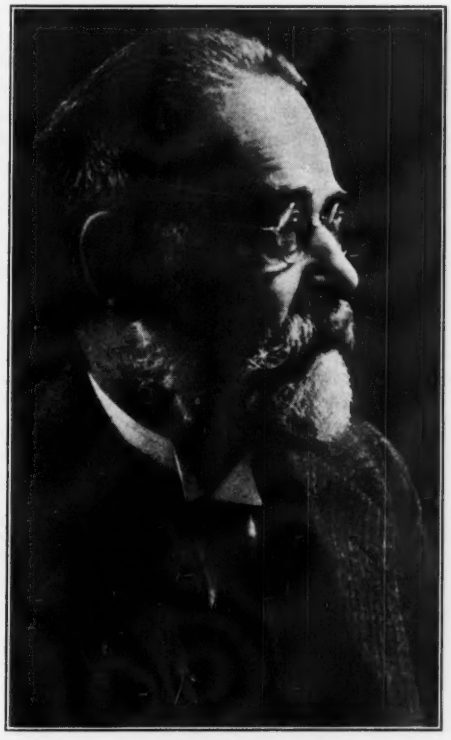
THE revival of scientific thought in the Occident did not emanate directly from the study of the Greek writers; on the contrary, the Arabs played an important intermediary rôle. At the Arabic universities in Spain, Arabic philosophy and medicine, astronomy and alchemy were taught and studied; at that period the Arabic literature held an authoritative position, its most important works were translated into Latin for use in the Western countries.

Unfortunately, the sources of information leading to a real knowledge of this intellectual relationship are so deeply buried that much laborious research will be necessary before the basic questions can be cleared up. How did the Arabs, originally wholly illiterate sons of the desert, acquire their highly developed science? By what routes did their science gain entrance into the Occident? Which of the texts that have been handed down are genuine, which are forgeries, which are revisions? What was the influence of these documents on the succeeding generations?

The leading Arabic personalities, their teachings and activities, were practically all forgotten in the course of time; only a few empty names and isolated anecdotes were passed on as mere traditions. Even the great Persian physician, philosopher, and chemist, Abu Bakr Muhammad ibn Zakariyya al-Razi, did not fare better, and only the specialists know of this important personage. Rhasez, as he is known in the West, was born in 860 at Ray, not far from Teheran, and died in 925 in his native city. Although he exerted a profound influence on both contemporary and later science, who today knows his works?

Julius Ruska, the indefatigable director of the Institute of the History of Science at Berlin, who, by reason of his wide knowledge of both philology and science, is especially fitted to study such problems, has contributed much toward answering the perplexing questions that envelop the al-Razi texts. In 1921, Ruska found in the University Library at Göttingen an old manuscript of al-Razi's principal work, *Kitab sirr alasrar* (The Book of the Secret of Secrets). There is no doubt that this is a genuine al-Razi text. Since then Ruska has made al-Razi the center of his researches. The manuscript of his book on al-Razi was completed three years ago but economic conditions made it impossible for him to secure the funds for the publication of his entire text, and so it became necessary for him to put it out in sections in order to rescue at least the most important

* Translated by Ralph E. Oesper, University of Cincinnati.



JULIUS RUSKA (1867–)

Professor at the University of Berlin, Director of the Institute for the History of Medicine and the Natural Sciences

After the completion of his fundamental education in mathematics and the natural sciences, Ruska entered the school service. As a young instructor he studied Oriental languages at Heidelberg. At the desire, and upon the advice of, Geheimrat Adalbert Merx, he published, as his doctoral dissertation, a mathematical chapter from a Göttingen Syrian manuscript. At the same time he translated and annotated the lapidary from the "Cosmography" of Zakarijâ ibn Muhammad ibn Mahmûd al-Kazwînî. Thereby he established the lines of his life's work.

At first he remained true to the school service and continued to deepen and extend his mathematical and scientific knowledge. In 1911 he transferred to the "high school"; his habilitation thesis treated the lapidary of Aristotle. In 1927 he was called to the directorate of the Research Institute for History of Science at Berlin.

results. Three parts have now appeared: *The Translation and Collation of al-Razi's "Book of the Secret of Secrets;"*[1] *The Book of Alums and Salts;*[2] *The Alchemy of al-Razi.*[3]

Al-Razi himself completed a catalog of his writings and this was handed down, in whole or part, in various biographic works. However, no worthwhile conclusions as to the great man's merits can be drawn from a mere listing of titles; a just verdict can only be reached by studying such writings of his as have been preserved. Unfortunately, not much of al-Razi's output is still extant, and up to the present only the following have been disinterred: *The Book of Propaedeutic Introduction;*[4] *The Book of Authoritative Quotations;*[5] *The Book of Secrets; The Book of the Secret of Secrets.* Manuscripts of the latter in the libraries at Leipzig, Göttingen, and at the Escorial have been compared and studied by Ruska.

The Book of the Secret of Secrets is divided into three main sections which treat of the description of substances, apparatus, and processes. The discussions are remarkably clear and thoroughly organized. The style of this introduction to chemistry is concise, the author treats his material objectively, and he uses very few cryptic designations. This strict adherence to his topic and avoidance of embellishments is never found among the Hellenistic alchemists and al-Razi must surely have acquired this admirable trait in the medical school of observation and from practice in the preparation of medicaments. As an example of al-Razi's excellent classification, Ruska[6] has chosen the arrangement of the third main section. Only the beginning will be given here:

Part I. The Processes of the Spirits and the Chapter of Calcination.

A. The Processes of the Spirits

(a) General Observations

(b) The Chapter of Mercury: (1) The preparation of mercury, (2) Concerning the refining of mercury, (3) The refining to whiteness, (4) The refining to redness.

(c) The Chapter of Sal Ammoniac: (1) Concerning the refining of sal ammoniac, (2) Concerning water of *martak*[7] and of red arsenic.

(d) The Chapter of Sulfur and the Arsenics: (1) Concerning the refining of the arsenics and sulfur, (2) Thorough washing, (3) Elucidation of washing, roasting, and boiling, (4) Bringing forth the essence of arsenic and sulfur.

Alchemy as presented by al-Rāzi must have been preceded by a development that did not occur on Greek soil, for he uses substances, such as sal ammoniac, that were entirely unknown to the Greeks, and which for the most part bear Persian names. The logically thought-out theory of alchemy, firmly rooted in experiment, must have grown up in Persian soil.

So far as can be judged from the few remaining genuine fragments of his writings and from other reliable sources, al-Razi seems to have exercised a considerable influence on his contemporaries in the East. The disciples of Egyptian alchemy with its pronounced devotion to mystical, allegorical doctrines naturally responded little if at all to al-Razi's teachings. However, in the Islamic Western countries, Spain and Morocco, al-Razi's work became the starting point of an extensive literature and of a widespread practice. Numerous European alchemists of the 11th to the 14th centuries were greatly indebted to both the form and content of the *Book of the Secret of Secrets.*

In the collected manuscript of the *Codex Speciale* of the *Biblioteca Comunale* of Palermo, Ruska found a complete Latin translation of the *Kitab sirr alasrar,* which corresponds in all parts to the Arabic text of the Göttingen manuscript, "MS ar. 95." On the other hand, the Paris manuscripts, 6514 and 7156, which heretofore were considered translations, are revisions and amplifications. The most important of all the revisions is the one contained in *Codex 933* of the *Libreria Riccardiana* in Florence. It dates from the 13th century and carries the title: *Geber de investigatione perfectionis magisterii; i. e.,* "Jabir on the investigation of the perfecting of the magistery." The new title is brought into harmony with the old one in an explanatory sentence, in which it is pointed out "secrets" are merely trade secrets, the meaning also used by al-Razi. "Liber hic noster, qui *secretum secretorum* intitulatur (de rerum praeparatione et complemento earum et perfecti operis investigatione), dividitur in tres partes. Quarum prima manifestat species, secunda vasa, tertia operationes specierum." "This our book, which is called *secret of secrets* (concerning the preparation of things and the completion of them and the investigation of the perfect work), is divided into three parts; the first sets forth the ingredients; the second, the apparatus; and the third, the treatment of them." This shows plainly that in its whole plan, the *Codex Riccardianus* agrees with the underlying Arabic work. Close inspection reveals that the chapters on substances and apparatus are dependent in all details on al-Razi's *Book of Secret of Secrets.* In the hastily edited Latin work, which in part is quite loosely put together, occur many expressions which at first seem puzzling, but these may be easily explained as efforts to translate words whose

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[1] RUSKA, J., "Übersetzung und Bearbeitungen von ar-Razi's Buch Geheimnis der Geheimnisse," *Quellen und Studien zur Geschichte der Naturwissenschaften und der Medizin,* **4,** Heft 3, 1–87 (1935), Springer, Berlin.

[2] RUSKA, J., "Das Buch der Alaune und Salze. Ein Grundwerk der spätlateinischen Alchemie," Verlag Chemie, Berlin, **1935,** 127 pp.

[3] RUSKA, J., "Die Alchemie ar-Razi's," *Der Islam, Zeitschrift für Geschichte und Kultur des islamischen Orients,* **22,** Heft 4, pp. 281–319 (1935), W. de Gruyter & Co., Berlin.

[4] STAPLETON, H. E. AND AZO, R. F., *Mem. Asiatic Soc. Bengal,* **3,** 57–94 (1910); **8,** 317–418 (1927).

[5] STAPLETON, H. E., has given extracts of this in *Mem. Asiatic Soc. Bengal,* **11,** 68 (1934).

[6] RUSKA, J., *Der Islam,* **22,** 295 (1935). Al-Razi knew four "Spirits," *i. e.,* volatile substances: mercury, sal ammoniac, sulfur, and arsenic (arsenic sulfide). He divided the mineral substances into six groups: spirits, metals, stones, vitriols, boraxes, salts.

[7] *Martak* = litharge.

meanings were not clear to the translator. In the third part, in the chief section on processes, the Latin text departs rather widely from the original; the arrangement and the wording are occasionally quite different. Some passages are considerably abridged and simplified, but in compensation, the theoretical portions are developed on much greater scale than in al-Razi's original. The better structure of the Latin sentences in the philosophical parts, and the scholastic style which is not at all reminiscent of the Arabic phraseology, point to an independent adaptation by a Christian alchemist. Ruska was able to show that certain recipes did not come from al-Razi but from Jabir ibn Hayyan. Evidence for the independent, further development of alchemy is furnished also by the extensive, coherent description of salts in the Latin text, subject matter unknown to al-Razi. The illustrations of common forms of apparatus are both surprising and instructive.

At the close of his study Ruska, with convincing arguments, advances the view that the editor of the *secretum secretorum* in the *Codex Riccardianus* was also the author of the *Summa perfectionis magisterii*. The author of the *Geber de investigatione perfectionis magisterii* or the editor of the *secretum secretorum* explicitly promised to put out a book on all the problems of alchemy, and this volume was to bear the title: *Summa*.[8] Stylistic variations in the independent parts of the *secretum secretorum* are repeated word for word, or almost so, in the *Summa perfectionis magisterii*. The coincidence of so many details cannot possibly be accidental.

The outstanding example of the texts that developed from al-Razi's works is the book: *De aluminibus et salibus*. Until quite recently this was held to be a genuine work of al-Razi, even though there is no mention of it in any of the catalogs of Arabic writings. Steele, in 1929, published the text on the basis of a Latin manuscript 6514 in the Bibliothèque Nationale at Paris and another manuscript (Arundel 164) in the British Museum.[9] An earlier and more complete form of the text is preserved in the *Codex Speciale* at Palermo. Ruska found extensive portions of an Arabic text in the Berlin manuscript, Sprenger 1908. He recognized, moreover, the supplement *De mineralibus liber* to the *Compendium Alchimiae* of *Joannes Garlandius*, which was printed at Basel in 1560, a second completely independent translation which had never before been recognized as such.

The Latin translations must have had older and more complete Arabic predecessors than the fragments in the Codex Sprenger 1908. The text of the *Garlandius* is the most complete. The Latin editions are patently entirely independent of each other; they vary in the terminology of chemical substances, apparatus, and processes, as well as in many phrases. The untranslated Arabic names, the geographical statements, the references to other writers, the use of the Divine name, the various ending formulas, the manifold divergences, gaps, and additions—from all of these it may be concluded that the author was a Moorish alchemist of the 11th to the 12th century. In any case, the book certainly did not originate with al-Razi; it does not conform in fundamentals to the undisputed works of the great Persian. Its unknown author was evidently well read and must have had practical experience. His compendium on alchemy was based on the writings of Jabir, of the Egyptian circle, and of al-Razi.

Ruska has translated the Arabic text into German and supplemented it on the basis of the more extensive *Garlandius*. His researches have set new milestones along the entangled road of the history of alchemy.

[8] RUSKA, J., *Quellen und Studien*, **4**, 78, 86 (1935).

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Courtesy of E. R. Schierz

GRAND DUKE LUDWIG OF HESSE-DARMSTADT UND BEI RHEIN

Born June 14, 1753—Died April 6, 1830

A patron of arts and sciences whose munificence made it possible for Liebig to study in Paris (1822-1824). To him, likewise, Liebig owed his appointment to the professorship at Giessen.

(From a lithograph by H. Backofen, *Kammer-Musikus* to the Hessian Grand Duke.)

DO STUDENTS THINK?*

HOSMER W. STONE

University of California at Los Angeles

THE writer sought the answer to this question from a class of more than one hundred students in beginning chemistry. The members of the class had previously studied high-school chemistry, or its equivalent. They were enrolled in the university as majors in medicine, engineering, chemistry, agriculture, etc.; 20 per cent. were women.

These students may be classified in three groups. Those who simply acquire information, but do nothing further with it, constitute the largest single group. Members of a second group not only memorize factual information, but also commit to memory certain logical thought processes which have been presented by the instructor or which have been given in the text. The third group is composed of that small minority—those who are really able to, and do, make use of the information they have acquired in logical thought processes of their own. This last group is frequently difficult to distinguish from the second group, but a way of doing this was discovered.

After the students had met problems relating to normality, density, and percentage composition in their laboratory work, the class was asked in a written quiz (April 5th) to solve the problem:

Calculate, showing method, the concentration in moles per liter of a 2.31% NH_3 solution, the density of which is 0.990 g. per cc.

The papers were corrected and returned. A satisfactory solution of the problem was presented to the entire class. It was pointed out that any one of the three factors, density, normality, or percentage composition could be calculated if the other two were known. The students were given a page reference to their text where four similar problems, with the normality unknown, were presented. The suggestion was made that the students, after solving for normality, assume density or percentage unknown and practice the solution. Further, the students were encouraged to ask questions at the time of explanation. Several students took advantage of this opportunity. On April 8th, the quiz contained the problem:

Calculate, showing method, the number of cc. of 20% HCl (density 1.1 g. per cc.) required to prepare a liter of 2 *N* acid.

The corrected papers were returned and explanations were again offered. On May 1st, the process was repeated with the problem:

55.1% H_2SO_4 is 16.3 *N*. Calculate, showing method, the density in grams per cc.

After eliminating arithmetical errors, it was found that not more than a third of the class were able to solve these problems. There was little noticeable improvement on repetition. The changing of the unknown factor from normality to density seemed to offset any gain which might have accrued from repetition.

Next, the class was challenged with the statistical results on the three problems and a statement that one such problem would be included in every written examination during the remainder of the semester. Further, it was stated that the instructor was curious to discover how many of the class could acquire an understanding of the principles involved.

On May 13th, the problem given was:

Calculate, showing method, the number of cc. of 40% sodium hydroxide solution, density 1.43 g. per cc., required to just neutralize 1 liter of 0.286 *N* HCl solution.

Eighty per cent. of the students solved this problem, but the instructor's attention was attracted to the fact that many students wrote down a formula in which they substituted the proper values to obtain a solution.

Accordingly, on May 27th, a quiz was given which included the question:

Explain how one could prepare a 5% HNO_3 solution from 15 *N* HNO_3 without determining the density.

This defied substitution in the formula and many students stated that the problem could not be solved. However, 9 per cent. did solve it; 9 per cent. could think.

On June 7th, the final examination was given and included the problem:

Calculate the weight in grams of 1 cc. of a 20% K_2CO_3 solution which is 3.48 *N*.

Most of the students turned in their papers before the time was up, yet only 34 per cent. were able to solve this problem. Apparently, the experience with the problem of May 27th had destroyed the confidence of some in the formula method.

It is the opinion of the writer that these students are fairly representative of those who enrol in beginning chemistry in this university and other institutions of this type. A similar experiment was carried out two years previously in the same course. That year, on April 7th, the class was asked:

How would you prepare a 100-cc. sample of 6 *N* nitric acid from commercial 68% HNO_3, which has a density of 1.42 grams per cc.?

The papers were graded and returned, an explanation

* Presented before the Division of Chemical Education at the ninetieth meeting of the American Chemical Society, San Francisco, August 21, 1935.

was presented to the class, and questions asked by the students were answered before the entire class. This was repeated with the problem given on May 3rd:

55.1% H_2SO_4 is 16.3 *N*. Calculate the density in grams per cc.

and another problem on May 19th:

18.4 *N* H_2SO_4 has a density of 1.5 grams per cc. Calculate the percentage of H_2SO_4 in the solution.

On June 3rd, the quiz contained the problem:

Calculate the number of cc. of 20% HCl (density 1.1 g. per cc.) required to prepare a liter of 2 *N* acid.

Counting problems which contained only arithmetical errors as correct, 58 per cent. of the class were able to solve this last problem.

On returning the papers after this fourth quiz, the whole matter, including statistical evidence on the ability of the class to solve the problem, was discussed and it was suggested that a similar problem would probably be included in the final examination. Two students asked for and received copies of the four problems which had been given.

The final examination on June 16th included the problem:

One cc. of 47% HNO_3 which is 9.8 *N* weighs —— grams. Fill in the blank space above the line with the correct number.

Only 30 per cent. of the class were able to solve the problem in spite of the fact that most of the class turned in their papers before the time was exhausted. The decrease of from 58 per cent. to 30 per cent. being able to solve this type of problem is in agreement with the observation that a better score is made when normality is used as the unknown than when percentage or density are unknown.

The project described above added a great deal of interest to the course. The instructor and his assistants found the reading of the papers much more interesting when there was such a score to be kept. The students developed lively curiosity as to the outcome of the experiment.

To differentiate clearly between those who simply memorize the logical thought processes and those who use them, is most useful. Certainly, there is no greater satisfaction to be had in teaching than may be derived from that rare circumstance where a student, in the consciousness of both student and instructor, sees the light and joins that select group, the logical thinkers.

On the CHEMICAL NATURE *of* TETANY*

DONALD E. BABCOCK

The Ohio State University, Columbus, Ohio

IF THE human organism is to be regarded as a purely chemical system, then it should be possible to apply the fundamental principles of equilibrium, ionization, phase rule, and electrokinetics to the conditions to be found in such a system. Among the pathogenic conditions traceable to purely chemical phenomena that may be interpreted on the basis of these principles is that of tetany.

The research of Weaver and Reed[1] indicated that the only changes in the blood associated with tetany, induced as a result of parathyroidectomy, were in the calcium and phosphate-ion concentrations in the blood. This is supported by the work of Schohl and Brown,[2] Linder and Harris,[3] Tsai and Hsu,[4] Benjamin and Gross,[5] Benznak,[6] Aub, Fuller, Bauer, and Rossmeisl,[7] and Csapó.[8]

The question as to whether the calcium, existing in diffusible or non-diffusible form, was an index of tetany or not seems to be a point on which authors disagree.[9,10]

In the urine, in cases of tetany, increased amounts of calcium and phosphates are found. Muscular activity depends on the chemical energy derived from the reactions of the phosphate complexes, which are split during muscular activity. This results in the production of phosphoric acid, which raises the phosphate-ion concentration in the blood. If the human system is not in a state of equilibrium after the introduction of these phosphate ions, changes will take place in order to attain such a condition. The particular ions which are of interest in cases of tetany are Ca^{++}, $PO_4^{\equiv}$, and $CaPO_4^{-}$.

The equilibrium in the body is that associated with liquids and solids either adjacent to or across membranes. The solid phase is the solid bony tissue. Bony tissues are essentially tricalcium phosphate minerals whose composition, according to Klement[11] and Gass-

* Presented before the spring (1935) meeting of the Ohio Academy of Science, Columbus, Ohio.

[1] WEAVER AND REED, *J. Biol. Chem.*, **85**, 281–8 (1929).

[2] SCHOHL AND BROWN, *ibid.*, **84**, 501–9 (1929).

[3] LINDER AND HARRIS, *Quart. J. Med.*, **23**, 195 (1930).

[4] TSAI AND HSU, *Chinese J. Physiol.*, **3**, 389–98 (1929).

[5] BENJAMIN AND GROSS, *J. Biol. Chem.*, **90**, 737–46 (1931).

[6] BENZNAK, *Biochem. Z.*, **236**, 362–71 (1931).

[7] AUB, FULLER, BAUER, AND ROSSMEISL, *J. Clin. Investigation*, **11**, 211–34 (1932).

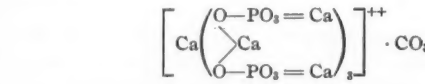
[8] CSAPÓ, *Monatsschr. Kinderheilk.*, **59**, 169–76 (1934).

[9] SNELL AND WALES, *Proc. Staff Meetings Mayo Clinic*, **5**, 17–20 (1930).

[10] GUNTHER AND GREENBERG, *Arch. Internal Med.*, **47**, 660–73 (1931).

[11] KLEMENT, *Z. physiol. Chem.*, **184**, 132–42 (1929).

man,[12] is essentially as follows:



which could be conveniently written $3Ca_3(PO_4)_2 \cdot CaCO_3$. Rosenburg, Hastings, and Morse[13] conclude from X-ray work that its essential structure is that of the apatite series and its composition may be considered as $CaCO_3 \cdot nCa_3(PO_4)_2$, where n varies from 2 to 3. Some authors[14] postulate the presence of $CaHPO_4$, combined in a complex manner with $CaCO_3$. However, it will be seen that this is probably not the case as may be noted in the later discussion of the calcium, phosphate, and H_2O equilibrium.

For the purpose of our discussion it matters little whether the bony tissue is a mono or polymineralic phase, whether apatite or not, so long as its essential composition is expressed mainly in terms of tricalcium phosphate, or solid solution of other materials in the same. This solid phase must be in equilibrium with dissolved Ca^{++} and $PO_4^{\equiv}$ ions. If there were not such an equilibrium, calcium phosphate would either dissolve out or be deposited depending on the condition present. Chemically described, the calcium and phosphate ion equilibrium is as follows:

$$\underset{\text{Solid bony tissue}}{Ca_3(PO_4)_2} \rightleftarrows \underset{\text{Dissolved ions}}{Ca^{++} + PO_4^{\equiv}} \rightleftarrows \underset{\text{Associated ions and other polyionic aggregates}}{CaPO_4^- + Ca_x(PO_4)_y^{z\pm}}$$

The chemical data on this equilibrium in pure H_2O at 25°C. have been worked out by Cameron and Bell.[15] The portion of their table of interest to this paper is as shown below.

CaO (*g. per l.*)	P_2O_5 (*g. per l.*)	*Solid Phase in Equilibrium with Solution*
0.145	0.381	
0.062	0.109	$CaHPO_4$ and $Ca_3(PO_4)_2$ solid solutions
0.049	0.088	
.....	.....	*Critical Line*
0.034	0.015	
0.587	0.013	$Ca_3(PO_4)_2$
0.789	0.012	

On recalculating this table in terms of phosphate ions and calcium ions the concentrations are as follows:

Ca^{++} (*g. per l.*)	$PO_4^{\equiv}$ (*g. per l.*)	*Solid Phase*
0.103	0.510	$Ca_3(PO_4)_2$
0.044	0.146	$CaHPO_4$
0.035	0.117	Solid solutions
.....	.....	*Critical Line*
0.024	0.020	
0.418	0.017	$Ca_3(PO_4)_2$
0.563	0.016	

[12] GASSMAN, *Z. physiol. Chem.*, **192**, 61 (1931).
[13] ROSENBURG, HASTINGS, AND MORSE, *J. Biol. Chem.*, **90**, 395 (1931).
[14] *Cf.* SHEAR AND KRAMER, *ibid.*, **79**, 105 (1928).
[15] CAMERON AND BELL, *J. Am. Chem. Soc.*, **27**, 1508–14 (1905).

Although this table is given for 25°C. and for pure water it is doubtful whether the condition with respect to these ions only will be appreciably changed under blood conditions at 37°C. The presence of complexes of either of these ions with such other substances as appear in the blood does not alter the validity of this assumption so long as the liquid phase is in equilibrium with a solid phase composed mainly of tricalcium phosphate, or a mineral phase whose composition is essentially $CaCO_3 \cdot nCa_3(PO_4)_2$. In terms of moles per liter:

Mole $[Ca^{++}] \times 10^3$	Mole $[PO_4^{\equiv}] \times 10^3$
2.63	5.37
1.13	1.54
0.89	1.23
.....	.....
0.62	0.210
10.66	0.178
14.25	0.168

The table shows that on either side of the *critical line* is to be found increasing solubility for calcium ions. Starting with the lowest indicated concentrations of phosphate ions it should be noted that as the concentration of phosphate ions is increased there is first a rapid reduction of the calcium-ion concentration for a very small increase in phosphate ions. In the human system this would correspond to the precipitation of calcium due to the slight increase over the normal phosphate balance. Upon further increase of the phosphate-ion concentration a point is reached where the calcium ion attains its minimum solubility. Beyond this point of minimum solubility the singular effect of increased phosphate-ion concentration is to increase the solubility of the calcium ions. This change is accompanied by a change in the nature of the solid phase in equilibrium with the dissolved ions. The chemical equilibrium may be indicated as follows:

$$\underset{\substack{\text{Solid bony tissue}\\ \text{up to 0.020 g.}\\ (PO_4^{\equiv})/l.}}{Ca_3(PO_4)_2} \overset{\text{No. 1}}{\rightleftarrows} \underset{\substack{\text{Dissolved}\\ \text{ions}}}{Ca^{++} + PO_4^{\equiv}} \overset{\text{No. 2}}{\rightleftarrows} \underset{\substack{\text{Associated ions;}\\ \text{mostly this form}\\ \text{above 0.020 g.}\\ [PO_4^{\equiv}]/l.}}{CaPO_4^-} \overset{\text{No. 2}}{\rightleftarrows} \underset{\substack{\text{New solid phase;}\\ \text{not present for}\\ (PO_4^{\equiv}) \text{ values}\\ \text{below 0.020 g./l.}}}{CaHPO_4}$$

Addition of phosphate ions at first decreases the concentration of calcium ions, shifting the equilibrium to the left along arrows No. 1. Above concentrations of 0.020 gram of $(PO_4)^{\equiv}$ per liter the calcium concentration increases instead of being diminished as might be expected. There is associated with this a change in the solid phase in equilibrium with the solution of the ions; the solid phase becoming a solid solution as indicated by Cameron, Seidell, and Bell. The shift in the equilibrium for the amounts of phosphate ions in excess of 0.020 gram per liter is along arrows No. 2.

It has been found that the administration of calcium salts is effective in the treatment of tetany. This is what one would expect from these data. It has been found by Cormel[16] that strontium prevents tetany but symptoms of strontium poisoning are present. So

[16] CORMEL, M., *Arch. fisiol.*, **29**, 159–80 (1930).

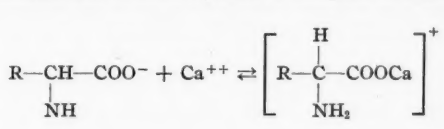
long as these symptoms persist the tetany is depressed. This, too, one would expect from the equilibrium data since strontium and calcium are closely related chemically. Magnesium should also lessen the severity of tetany by a similar process as it too belongs to the same family in the periodic table.

The complexes of the phosphate ions with glucose are well known, and the addition of glucose to a solution would induce the formation of glucose phosphates and also ease the conditions of tetany. These are the conditions found by E. P. and D. R. McCullagh.[17] It is fitting to point out that in every case the singular effect of the treatment was to decrease the available phosphate ions not associated in complexes. Probably the agent best suited to relieve these conditions at the present time would be calcium gluconate.

In biological researches up to the present time no direct correlation between the calcium and phosphate-ion concentrations for the production of tetany[18] has been established.

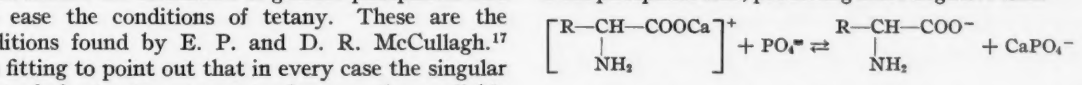
A threshold value for calcium was found and reported by Aub, Fuller, and others.[7] This is also to be expected, for the changes in the calcium concentration are many fold that of the phosphorus, and pass through a minimum, while the concentrations of the phosphate ions do not pass through any corresponding minimum point. The phosphate-ion concentrations are only progressively increased or decreased.

The amino acids form complex ions with calcium. One negative amino acid anion may combine with one calcium ion to form a positive complex as indicated:



This is another side of the equilibrium involving calcium. The amount of these associated positive ions present depends on the concentration of the available calcium ions. If, however, the concentration of the available calcium ions is diminished by the presence of larger concentrations of available phosphate ions, then very little of the complex can be formed. At the same time the greater part of the dissolved calcium will be in the associated complex form, as $CaPO_4^-$ or dissolved calcium acid phosphate. Bernhard and Beaver[19] and Perette[20] found that the calcium was in the negative ion in such phosphates and moved toward the anode in their electrokinetic determinations. This is in agreement with the $CaPO_4^-$ interpretation.

The body cells are negatively charged with respect to their surrounding medium. This potential difference will materially affect ionic diffusion through membranes or capillaries. The diffusion of positive ions into cells would be aided by the potential difference[21] and the diffusion of negative ions deterred. When the concentration of phosphate ions is increased, as in tetany, the normal equilibrium of the system will be disturbed, the normal calcium-amino acid or calcium-protein complexes will give up some of their calcium to the phosphate ions, producing more negative ions.



The $CaPO_4^-$ may pick up an H^+ ion or other monovalent ion, forming a soluble salt, and pass out of the urinary tract.

Under these conditions and in the presence of large amounts of $PO_4^{\equiv}$ the calcium and phosphate are both lost from the system in appreciably increased amounts and the pathological condition of the bony tissue is explained by the reaction:

$$Ca_3(PO_4)_2 + 2PO_4^{\equiv} \rightleftarrows 3\,CaPO_4^-$$

Thus chemically, on the basis of the general principles of equilibria, a theoretical explanation has been given, which accounts for some of the chemical effects involved in the treatment and pathology of tetany. In this discussion many aspects of the problem have been omitted due to lack of sufficient research and data. However, the picture as presented has within itself no contradiction, and, as has been shown, the literature is in accord with these interpretations. The use of thermodynamic concepts and treatment has been avoided in the interest of simplification.

Any biological problem is fraught with many difficulties—this one in particular with the apparently unexplained relation between the effects of vitamin "D," lymph extract, and parathyroid compounds in their influence on tetany and their use in its treatment. When the nature, structure, and activity of these are known, they too may find easy correlation in this picture.

Among other things relevant to this discussion are the agglomerating and peptizing effects of the ions mentioned, since the state of aggregation is a factor in the surface energy of a system.

It is hoped that this paper has indicated the necessity of knowing clearly the dependent and independent variables of a given biochemical problem, and that the introduction of such complex variables as parathyroid compounds, vitamin D, or serums, serves to confuse unless each of their component activities is known and recognizable.

Let us build our picture slowly but surely into a uniform whole and remember that it is only by apparent non-agreement of facts and observations that anything is learned.

[17] McCULLAGH, E. P. AND D. R. McCULLAGH, *J. Lab. Clin. Med.*, **17**, 754–72 (1932).
[18] McLEAN AND HASTINGS, *J. Biol. Chem.*, **108**, 285–321 (1935).
[19] BERNHARD AND BEAVER, *ibid.*, **69**, 113 (1926).
[20] PERETTE, *Boll. soc. ital. biol. sper.*, **8**, 498–500 (1933).
[21] FRANCE AND ORT, *J. Phys. Chem.*, **33**, 1374–85 (1929).

VALENCE *and* MOLECULAR STRUCTURE

JOHN DEVRIES

Knox College, Galesburg, Illinois

This article deals with the general problem of modernizing the course in elementary chemistry. A valence bond is defined as being composed of two electrons whose spins are paired. The different types of possible valence bonds are defined and the applications and advantages of approaching our problems in teaching valence and molecular structure from this viewpoint are offered. A modification of the definition of valence offered by Flood in the JOURNAL OF CHEMICAL EDUCATION, **12,** *132 (1935) to include the different types of valence bonds is suggested.*

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THE question of what to teach the student of chemistry concerning valence and the structure of molecules has interested the author for some time. An examination of most elementary texts reveals a brief discussion of such topics as radioactivity and radium disintegration, positive-ray analysis, and usually a discussion of the Bohr theory with its electron orbits, a theory which prohibits the formation of even such an elementary substance as molecular hydrogen. One finds but little concerning the nature of the valence bond, and frequently the discussions attempt to carry over into the field of inorganic chemistry the valence theories of the organic chemist without modifying them. An examination of the average structural formulas in most elementary texts substantiates this statement. Flood (*1*) in a recent article errs likewise when he defines valence on the basis of typical C—C- or C—H-like bonds and defines the valence of positive or negative ions as a number representing the positive or negative unit charges associated with the ion. Although the latter part of his definition is correct, strict adherence to the first part leads him into difficulty. His statements that chlorine in the perchlorate ion has a valence of four and that sulfur in the sulfate ion also has a valence of four are illustrations of the inorganic chemist applying the valence theories of the organic chemist and failing to distinguish between the different types of bonds in the molecule. Everyone knows that when the organic chemist states that carbon has a valence of four he means that we can attach other atoms to carbon by means of four definite valence bonds.

G. N. Lewis and his students have given us much of the material which could well be used as a basis for teaching the structure of molecules and for unifying the valence theories. Lewis (*2*) defines a valence bond as a bond composed of a pair of electrons whose magnetic moments neutralize each other or, in terms of the newer theories, the bond is composed of two electrons whose spins are paired. By a spinning electron is meant one which spins on its own axis with a great enough velocity to give it a magnetic moment equal to the Bohr magneton. The concept of the pairing of two electron spins is in agreement with the Pauli exclusion principle, which states that there cannot be two electrons in the atom which have the same values for all the four quantum numbers. This gives us the possibility of two electrons having the same principal quantum number, n, the same amount of angular orbital momentum, l, and the same magnetic quantum number, m_l, but different spins. For example, in helium where the values of n, l, and m_l are the same for both electrons we have a pairing of the electron spins which prohibits compound formation. Approximately 456,000 calories per gram atom are required to unpair the electron spins and raise the principal quantum number to two. This explains why helium does not ordinarily form compounds. Two unpaired electrons in different atoms, however, may be readily coupled together to form a valence bond and the electrons then oscillate between the atoms and appear to be part of both. In the case of atoms having an odd number of electrons each atom must contain at least one free magneton, and this explains why nitrogen and chlorine, for example, exhibit odd-numbered valences more frequently than do even-numbered atoms, which usually have an even-numbered valence. Lewis refers to this pairing of electrons to form a valence bond as the rule of two. Although it is not advisable to teach the fundamental concept of the spinning electron to an elementary student, the concept that a valence bond is composed of two electrons should not be difficult to accept. The student who is intelligent enough to wonder how, on the basis of Coulomb's law, two electrons can exert an attraction for each other rather than a repulsion should also be intelligent enough to understand an explanation of magnetic attraction in the electrons. The physics course in which he learned Coulomb's law will also have taught him Oersted's law that a flow of electricity (movement of electrons) causes magnetic phenomenon.

The rule of four, which states that we can attach four definite valence bonds or groups to the central atom, and the rule of eight, which states that in any stable, closed molecule each atom may be surrounded by a maximum of eight electrons, can be readily presented.

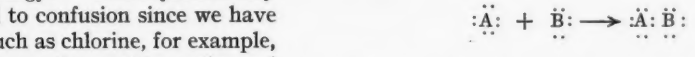
For a complete discussion of these rules and exceptions the reader is referred to Lewis (*2*) and Rodebush (*3*).

Another concept which is vital for the student to know is the varying attraction which different atoms have for electrons. We usually define an electropositive element as one which tends to give up its electrons and an electronegative element as one which exerts a strong attraction for electrons. Rodebush (*3*) has suggested that this varying attraction of the atoms for electrons be expressed in terms of the field about the atom. He points out that the terms electropositive and electronegative arose before the discovery of the electron and that these terms have been used in so many ways in connection with the properties of molecules that they are ambiguous. The field in the neighborhood of all atoms, with the exception of the inert gases, is positive, that is, the atoms all attract electrons, but in a varying degree. While it is not possible to compare quantitatively the atoms in different groups, an approximate measurement of the "positivity" of the atoms in a single group may be found by dividing the number of valence electrons by the number of shells. The atom will be more positive as the value of the effective nuclear charge increases. Thus chlorine is less positive than fluorine, but in comparison with sodium it would be considered strongly electropositive. To sum up his argument, Rodebush states, "This is contrary to the current usage in inorganic chemistry where chlorine is usually termed negative or electronegative, but the current usage arose before the discovery of the electron and there seems to be no good reason for adhering to an illogical terminology." The objection may be raised that this will lead to confusion since we have always regarded elements such as chlorine, for example, negative, since they migrate to the positive pole, and other elements positive, since they migrate to the negative pole. However, we are then dealing with ions and it can readily be pointed out that the element has either gained or lost an electron and hence has formed a charged ion. The author has found this concept to be rather teachable and not confusing after the student has mastered this approach.

If we consider the valence bond to be composed of two electrons whose spins are paired, rather than a rigid, unyielding link, we have the possibility of a number of different types of bonds. The first type is sometimes called a polar bond and occurs when an atom takes an electron completely away from another atom and forms an ion. Rodebush (*3*) has pointed out that this appears to be a misnomer and that the term polar molecule is more suitable in this case. Langmuir, in developing his electronic theory of chemical combination, called this type of bond or union "electrovalency" and it seems desirable to speak of this type of combination in the latter way.

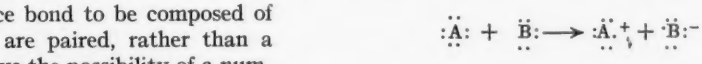
A second type of combination results when each element contributes one electron in the formation of the bond and the two electrons then oscillate between the atoms, appearing to belong to both. In some cases the electrons shift toward one atom in order to give it a resultant negative charge and the other a resultant positive charge, although it is not correct to speak of any atom having an integral number of units of charge unless one of the atoms takes the electrons completely away from the other and forms an ion. This type of combination has been termed "covalency" by Langmuir and is also designated occasionally as a non-polar bond. In general, according to the Fajans theory, ions of high valency, whether positive or negative, favor the formation of covalent rather than electrovalent linkages. When the cation is small and the anion large an electrovalency tends to pass over into a covalency. Beryllium chloride, for example, exhibits mainly a covalent linkage in the fused state, as indicated by its resistivity, while in water solution, although somewhat hydrolyzed, it becomes a fairly good conductor, indicating the presence of an electrovalency. The metals in the A sub-group of Group I in the periodic system tend to form electrovalent compounds readily, since they need to lose only one electron to form an outside shell of eight electrons.

A third type of combination, which Sugden has termed the semipolar bond, occurs when a molecule or ion contributes both of the electrons in forming the bond. This type of bond is a special type of covalency which Sidgwick has termed a coördinate covalence. There are two mechanisms proposed to illustrate the formation of this bond. The first suggests that the two electrons are simply donated by the one molecule or ion and the electrons are then shared between the two, thus:



Here A is termed the donor and B the acceptor molecule or ion. A cannot be an atom, since if it were it would be an inert gas. Such a molecule, AB, is expected to have a certain amount of polarity; hence the term semipolar bond.

Another viewpoint suggests that an electron is first transferred from A to B to yield A^+ and B^-, thus:



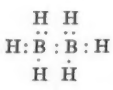
The two particles now unite by means of a covalent bond. Looking at it from this point of view the semipolar bond would be composed of one electrovalent and one covalent bond and would appear to be a type of double bond. The bond is usually represented either $A^+—B^-$ or $A \rightarrow B$, the arrow indicating the direction of the transferred electrons.

The question of the proper name for this type of bond is still a matter of debate. As pointed out before, Sidgwick suggests the name "coördinate covalency," and recently W. A. Noyes has suggested the term "semi-ionic" valence. The author prefers the term semipolar bond, since Sidgwick's term is really an application of Werner's coördination valency. Werner deals with the union of two substances capable of sepa-

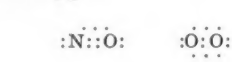
rate existence, and represents the bond by an arrow, while Sidgwick applies the term to all semi-polar linkages. It would be less confusing if we restricted the term coördinate covalence to Werner's original meaning, since the normal semipolar bond is not readily broken while in the coördinate type it can be broken more easily, since the two molecules are capable of separate existence. The definition suggested by Noyes also implies a concept of polarity and may be substituted for the term semipolar bond if so desired.

It may be added, parenthetically, that a semipolar bond behaves physically as though it were a single bond, although it is permissible to count it numerically as two linkages when computing classical valency. The average value of the mean restoring forces for various linkages as calculated from molecular spectra data indicates that there is really no fundamental difference, stereochemically at least, between an ordinary covalency and a semipolar or coördinate covalency. Hence, in writing structural formulas for inorganic compounds we should not merely present the usual formula. For example, the formula H—O—N$\langle^{O}_{O}$ leads one to believe, erroneously, that two of the oxygens in nitric acid are doubly bonded. A more exact formula would be H—O—N$\langle^{O}_{O}$.

These three types of bonds, namely, electrovalent, covalent, and semipolar, do not exhaust the list. Pauling (*4*) has calculated from the standpoint of wave mechanics the possibility of one-electron and three-electron bonds. For the structure of diborane he suggests



although Lewis suggests that the six electron pairs oscillate between the seven possible positions.* The three-electron bond has been suggested in the case of nitric oxide and oxygen.



However, a discussion of these types of bonds is beyond the scope of this paper.

The applications which can be made from the above rules and definitions are many and varied. A consideration of a few uses should be sufficient.

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* Farkas and Sachsee (*12*) have demonstrated by a series of experiments at 196°, 293°, and 373°K. that the ground level of B_2H_6 must be diamagnetic. These results tend to substantiate the suggestion made by Lewis that the six electron pairs oscillate between the seven possible positions since such a compound would be diamagnetic. If Sidgwick's and also Pauling's proposed structure involving two hydrogen atoms attached by singlet linkages were correct, the compound should be paramagnetic. It should be added that the experiments of Farkas and Sachsee do not exclude the possibility of a paramagnetic excited state above the diamagnetic ground state.

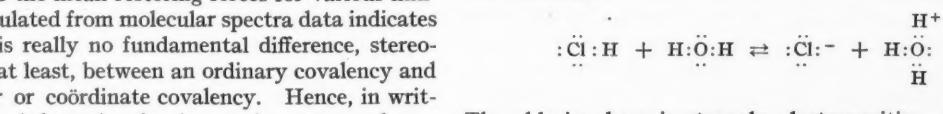
Kilpatrick (*5*) in a recent article discusses the subject of acids, bases, and salts. Among other things, he points out that the ionic equilibrium for hydrochloric acid in water should not be written as is usually done, *viz.*,

$$HCl \rightleftarrows H^+ + Cl^-$$

but in this way,

$$HCl + H_2O \rightleftarrows H_3O^+ + Cl^-$$

The question arises, if we wish to incorporate this in our teaching, would it not be desirable to offer an explanation for this reaction? If we write the formulas indicating the electron arrangement in the elements we have the following:



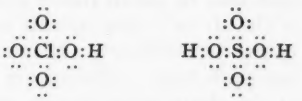
The chlorine here is strongly electropositive, *i. e.*, it seeks to pull electrons to itself, thus liberating the hydrogen which can attach itself to the oxygen of the water molecule by means of a pair of electrons donated by the oxygen, and form an oxonium ion by means of the hydrogen ionic bond.

If we consider the other acids of chlorine we can readily see why the oxygen acids are weaker than the simple hydrogen acid. In picturing the following condition

the question naturally arises why a hydrogen should leave one oxygen to attach itself to another. The answer is that hydrogen does not have much tendency to do this unless there is a strain producing shift of electrons within the molecule. In the case of hypochlorous acid in water

the hydrogen is liberated, since the chlorine tends to pull the electrons to the left. However, the electrons are not pulled as far away from the hydrogen as they are in hydrochloric acid and we find that hypochlorous acid is a weaker acid than hydrochloric acid in water solution. The addition of more oxygens, by means of semipolar bonds, produces a greater shift of electrons in the molecule away from the hydrogen and causes the acid to become stronger, *i. e.*, hydrogen ions are more easily liberated. A semipolar bond produces more strain than a normal covalent bond and less strain than a double bond. As pointed out before, Flood (*1*) does not distinguish between these bonds in his definition of valence. The author feels that if we can teach students to regard structures in this light we shall be able to explain more properties of compounds to them than our present system permits us to explain. For a detailed discussion relative to the strength of acids and bases the reader is referred to Lewis (*2*), Latimer and

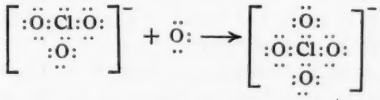
Rodebush (*6*), and N. F. Hall (*7*). Our pictures for perchloric acid and sulfuric acids then should be



Sugden (*8*) has confirmed the fact that we have two semipolar bonded oxygens in sulfuric acid.

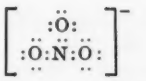
The concept of acidic and basic groups follows quite naturally if we view molecules in the light of their electronic structure. Kilpatrick (*5*) in his recent article has summed up the theory suggested independently by both Lowry and Bronsted (*9*) in 1923 for defining acids, bases, and salts. An acid is defined as a donor or source of protons, a base is defined as a proton acceptor or a substance which can unite with protons, and a salt is defined as a system which is built up from oppositely charged ions which do not neutralize each other. Since the facts have been clearly stated in the two articles cited, they need not be enlarged upon here.

Oxidation-reduction reactions are also explainable by means of this method. W. A. Noyes (*10*) suggests the possibility of three types of oxidation. The first type involves an actual transfer of electrons as found, for example, in the reaction of sodium with chlorine. The second type he calls oxidation by positive hydroxyl. Hydrogen peroxide separates into a positive hydroxyl, $H:\ddot{O}^+$, and a negative hydroxyl, $:\ddot{O}:H^-$, in the same way that chlorine separates into positive chlorine, $:\ddot{Cl}^+$, and negative chlorine, $:\ddot{Cl}:^-$, in reacting with water. This type explains the oxidation of hypochlorous acid to chloric acid. Since the equations are written electronically in the original article by Noyes (*10*) they will not be repeated here. The third type is called oxidation by semipolar oxygen atoms. In oxidizing the chlorate ion to perchlorate ion we may consider the transfer of an electrically neutral oxygen from one atom to the other, thus



The oxidation of alcohols by agents which contain semipolar oxygens, such as nitric acid and potassium permanganate, is probably of this type. This leads to a redefining of the term oxidation-reduction. As pictured above it is hardly correct to say that oxidation is a loss of electrons, since the two electrons needed to attach the fourth oxygen in potassium perchlorate have not been taken up wholly by the oxygen. Only in the case of electrovalency do we get a complete loss of electrons in an atom. When we say that chlorine in potassium perchlorate gains eight electrons when reduced to the chloride state we really mean that the chlorine has sole possession of its original seven electrons and obtains another due to the electrovalent bond formed with potassium. Oxidation-reduction should be defined in terms of the number of electrons which are donated or accepted in the sharing between the atoms if we wish to make the definition exact, for only in the case of ionized substances do we have an actual gain or loss of electrons. This picture should not spoil our method of balancing oxidation-reduction equations by the electron method, where the change in valence of the elements is considered.

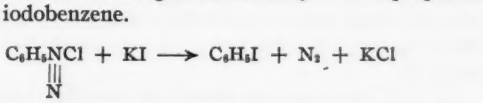
Bennett (*11*) in a recent article runs into much the same type of difficulty in discussing the nitrate ion as Flood (*1*) does in discussing the perchlorate ion. His picture of the nitrate ion shows only six electrons around the nitrogen,



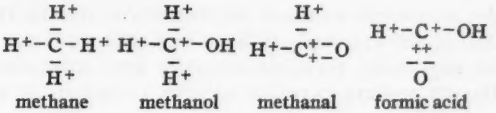
The formula should show one double-bonded and one semipolar bonded oxygen. The other oxygen is held on by a covalent bond. In discussing the reduction of nitrogen in the nitrate ion to nitric oxide Bennett states that one may assume that the nitrogen gains three electrons in this process. It would be more accurate to state that in nitric oxide the nitrogen shares three electrons less than it does in nitric acid, *e. g.*,

The electrons contributed by the nitrogen are represented by x.

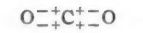
Another reaction, although possibly not of the greatest importance, which can be explained on the basis of the above postulates is the order of activity of the halogens. The student is taught that fluorine is the most active and iodine the least active of the halogens, chlorine and bromine occupying the intermediate positions. As proof for this statement he is taught the reaction between potassium iodide and chlorine. However, in studying the chlorates he discovers that iodine can displace the chlorine. If he were taught that the activity is really a measure of the ability to attract electrons, the reactions are logical, since chlorine in both of the above cases forms the negative ion, indicating it to be more electropositive than iodine. The same type of reaction is found in organic chemistry in the preparation of iodobenzene.



As a final application, the states of oxidation of carbon, indicating the relative degree of polarity, can be represented as follows:



methane methanol methanal formic acid



carbon dioxide

In the case of methane we have four covalent bonds. In methanol, the oxygen of the hydroxyl group pulls the electrons in closer to itself and leaves the carbon positive with respect to it. In methanal the oxygen exerts still more pull and, since we have a true double bond here, we have the state of oxidation as shown. The structures of formic acid and carbon dioxide explain themselves.

The objection may be raised that a concept as comprehensive as the above is too difficult for mastery in a first-year course in chemistry. It is not being proposed with any such hope. The author does believe, however, that the above point of view will enable the advanced student to understand more clearly the structure and properties of a host of inorganic compounds.

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The DETERMINATION *of* CHROMIUM *in* CHROMITE

J. P. MEHLIG

Oregon State College, Corvallis, Oregon

THE most important ore of chromium is a compound of iron and chromium known mineralogically as chromite, having a composition corresponding to the formula $FeO \cdot Cr_2O_3$. Although chromite cannot be dissolved in acids and is not easily decomposed by fusion with alkali carbonates, it is readily decomposed by fusion in an iron or nickel crucible with sodium peroxide, which oxidizes the iron to ferric oxide and the chromium to chromium trioxide. The latter then combines with sodium oxide to form sodium chromate. After solution of the sodium chromate in water it has been the general practice to filter off the iron residue before acidifying the solution. The resulting filtrate of dichromate solution is reduced by adding excess ferrous ammonium sulfate and the excess of the latter is titrated with standard potassium dichromate solution.

Several years ago two important modifications of this procedure were introduced by the writer in his classes in quantitative analysis at Oregon State College and have subsequently been in regular use. Since nickel crucibles were not available and since the use of iron crucibles introduced so much additional iron residue that filtration was extremely difficult and tedious, if not almost impossible, porcelain crucibles were substituted. Although sodium peroxide attacks porcelain, it was found that a successful fusion could be made by placing the crucible inside a slightly larger porcelain crucible. The outer crucible protects the inner one from overheating. In case the fusion mixture should go through the inner crucible, the outer one prevents loss of the determination. The inner crucible may frequently be used for several fusions. The outer one of course will last indefinitely. Lundell, Hoffman, and Bright (*3*) have recently suggested fusion in porcelain, but they do not use the protecting outer crucible.

The second modification consisted in the omission of the filtration before acidification of the chromate solution. As all the iron is in the ferric condition, its presence in solution during the reaction between ferrous ammonium sulfate and the dichromate is not harmful.

The determination of chromium in chromite is such an excellent one to give students needed experience that it has seemed advisable to present the detailed directions for the procedure together with results that have been obtained by its use.

PROCEDURE

Titration mixture.—Prepare a solution containing 150 ml. of concentrated sulfuric acid and 150 ml. of phosphoric acid, sp. gr. 1.7, in 1000 ml. (*2*).

Diphenylamine indicator.—Dissolve 1 g. diphenylamine in 100 ml. concentrated sulfuric acid.

Weigh accurately about 0.25 g. of the finely powdered ore and transfer to a 25-ml. porcelain crucible. Weigh upon a watch glass on a rough balance 5 g. sodium peroxide, selecting only the yellow material, as any white crust is sodium carbonate or hydroxide resulting from the decomposition of the peroxide by the air. Pour about three-fourths of the peroxide upon the ore sample in the crucible and mix well by stirring with an iron nail. Pour the remaining peroxide on the surface of the mixture. Leave the nail in the crucible.

Place the crucible in a larger porcelain crucible on a clay triangle and raise the temperature *very slowly* to the melting point of the flux, using a low flame and holding the Bunsen burner in the hand. The mixture should be entirely liquid after about ten minutes. Maintain this fusion for ten minutes more, stirring constantly with the nail, which is held by crucible tongs. Do not heat above moderate redness. Allow the mixture to cool until a crust forms on top, add 1 g. sodium peroxide, and fuse again for 5 minutes. Let cool, place the inner crucible and the nail in a 400-ml. beaker, and, keeping the beaker covered with a watch glass, add 75 ml. water. (Note 1.) The outer crucible should not be placed in the beaker unless some of the fused material has come in contact with it. When the evolution of gas has ceased, rinse off and remove the nail. (Note 2.) Boil ten minutes to decompose the excess peroxide (Note 3), stirring to prevent bumping, or digest on a water bath for 30 minutes, stirring occasionally.

Add just enough 25% sulfuric acid to dissolve the yellowish brown precipitate. (Note 4.) A fleecy white precipitate of silicic acid may remain, but does no harm. There should be no dark particles of undecomposed ore, and the solution should be orange-colored. Add 25 ml. more of the sulfuric acid and boil ten minutes to remove all dissolved oxygen, stirring to prevent loss by bumping. (Note 5.) The crucible may be removed here if desired. (Note 6.) The volume of the solution should be about 170 ml. Weigh accurately 0.2 g. more than enough pure ferrous ammonium sulfate to reduce the dichromate, upon the assumption that the ore is pure chromite, add it to the cold dichromate solution, dissolve, and mix well. Add 30 ml. titration mixture (Note 7), 3 drops of diphenylamine indicator, and titrate immediately the excess ferrous salt with 0.1 *N* potassium dichromate solution. (Note 8.) At the endpoint the last bit of green is displaced by blue. Calculate the percentage of chromium in the ore.

Notes. 1. In the treatment of the fused mass with water the volume of the latter is purposely held down to avoid the necessity of subsequent evaporation.

2. If the nail were not removed before acidification, the ferrous sulfate formed would reduce some of the dichromate from the ore and cause a negative error.

3. The excess sodium peroxide must be completely decomposed by boiling before the solution is acidified to prevent the formation of hydrogen peroxide, which would oxidize the dichromate to perchromic acid, which is especially unstable in strong acid solution, giving Cr^{+++} ions. This action would cause a negative error.

4. Especial care must be taken in acidifying the basic solution not to add more than just enough acid to dissolve the iron precipitate. If too much sulfuric acid is present during the final titration, it partially destroys the diphenylamine and the endpoint is very uncertain or impossible of detection. Best results are obtained when the volume of 25% sulfuric acid added after neutralization is held to 25 ml.

5. Thorough boiling of the acidified solution is necessary to remove dissolved oxygen produced when the excess sodium peroxide was decomposed by the water. Unremoved oxygen would oxidize some of the added ferrous salt, causing a positive error.

6. Most students prefer to let the crucible remain in the solution because the white background is an aid in detecting the endpoint of the titration.

7. Thirty ml. of titration mixture rather than the 15 ml. usually called for in iron titrations is used because of the large amount of iron present.

8. The volume of the solution at the start of the titration must be 200 ml., as this is the volume used when the potassium dichromate solution is standardized (*4*). It has been shown by Eppley and Vosburgh (*1*) and by Willard and Gibson (*6*) that the result of a dichromate-ferrous sulfate titration is influenced by acidity, volume of solution, and concentration of dichromate. Their results show variations of more than 0.5% when these factors are varied. It is obvious, therefore, that it is necessary to make the titration in a determination under the same conditions of acidity and volume obtaining in the standardization, using preferably about the same volume of titration solution.

RESULTS

The writer has previously reported (*5*) a few student results for chromium in chromite. The method used for that work was not so carefully standardized as is the present one. The accompanying table shows the results that have been obtained during the past few years by students at Oregon State College following the procedure given above. In the interests of space conservation, only class averages are recorded. Individual student figures are averages of duplicate determinations and represent ordinary classwork.

STUDENT ANALYSES FOR CHROMIUM IN CHROMITE

Sample No.	*No. Student Determinations*	*Cr Content** %	*Avg. Value Reported* %	*Avg. Deviation* %
1	16	32.35	32.38	0.19
2	27	31.42	31.53	0.19
3	25	28.22	28.28	0.20
4	20	22.86	22.74	0.19
4	12	32.42	32.44	0.15
6	13	23.23	23.28	0.17

* Determination of commercial laboratory supplying sample.

A study of the table indicates that the method is satisfactory. Students who carry through the process carefully get good results on their first attempts.

SUMMARY

Chromite ore may be satisfactorily fused with sodium peroxide in a porcelain crucible if an outer crucible is used for protection.

It is not necessary to filter the ferric oxide-hydroxide residue before acidification of the chromate solution.

The volume of the solution at the start of the titration should be close to 200 ml. and the amount of sulfuric acid present must be carefully controlled.

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The MAGNETO-OPTIC METHOD *of* CHEMICAL ANALYSIS

III. LOCATION OF MINIMA AND QUANTITATIVE ANALYSIS

STANCIL S. COOPER WITH T. R. BALL

Washington University, St. Louis, Missouri

IN THIS, the concluding article in this series on the magneto-optic method of chemical analysis,* the actual procedure followed in the solution of a problem with the Allison apparatus will be given in order to show how many difficulties encountered in the use of the set-up are overcome. It is the belief of the authors that too often the many difficulties met with in a chemical problem never find their way into print. That this is necessarily the case is obvious when one considers the large number of articles which are published. Because of several failures with the apparatus caused chiefly, as we believe, by set-ups which were not functioning properly or by observers who did not appreciate the many difficulties involved, it is advisable to present the method used in carrying out a problem involving the use of the apparatus. The question has been frequently asked, "How does one satisfy himself that certain minima are those of a particular compound and not those of an impurity?" This question, we feel, can best be answered by giving the actual procedure used in locating the minima for certain substitution products of benzoic acid. Salicylic acid will be used to illustrate the method.

LOCATION OF THE MINIMA

Elimination of Impurities in the Solvent.—The water used was doubly distilled, *i. e.*, ordinary distilled water was redistilled in an all-pyrex apparatus and received in pyrex flasks. The containers for this water were steamed for several hours with an all-pyrex steamer and finally rinsed several times with the doubly distilled water before they were used. The observation cells were scrubbed with brushes, in tap water, in ordinary distilled water, and finally in pyrex-distilled water. These three brushes were never interchanged and were kept covered in glass cylinders to guard against outside contamination. This method of removing impurities from the walls of the cells is essential. A cell was not used for a second solution until the ends had been removed and it had been thoroughly scrubbed and rinsed. All the volumetric flasks and containers for solutions were pyrex with ground-glass stoppers. Every flask was thoroughly steamed and rinsed before it was used. Flasks in which solutions were stored were covered and placed in wooden or glass cases to prevent contamination by dust particles. Pipets were washed originally with cleaning solution and then rinsed by allowing pyrex-distilled water to flow through them for several minutes. This washing with the doubly distilled water was always carried out when the pipet was to be used for a second solution. Solutions were prepared, dilutions were made, and cells were filled under an overhead glass shield.

In order to prevent the appearance of minima resulting from contaminations, the doubly distilled water was carefully tested over the regions of the scale to be examined later when the solutions were under observation. If minima appeared, the cell containing the water was discarded and another used. If minima still appeared, the water was either discarded or redistilled. This process was continued until the water was shown to be suitable for making the solutions. The minima for magnesium compounds are always present in water which has been exposed to the atmosphere about the apparatus for a considerable time. The magnesium oxide from the spark-gap contaminates the solution. This may be overcome, however, by using freshly distilled water and making observations quickly or by keeping the observation cell closed during the analysis.

Minima for Salicylic Acid.—Exhaustive research with the apparatus has revealed that: (1) a compound continues to produce its characteristic minimum or minima until its concentration has been reduced to a few parts in 10^{12} of solvent, and (2) in a series of compounds, with anion constant, the scale readings are direct functions of the equivalent weights of the cation and, with cation constant, inverse functions of the combining equivalents of the anion. Consequently, in attempting to establish minima positions for a compound it is necessary first to determine whether the solvent contains substances which produce minima in the region of the scale to be examined, and second to use a concentration of about one part in 10^{11} of solvent in order that impurities introduced with the compound may not produce minima. The close adherence to the procedure for the elimination of impurities from the solvent is essential in this phase of the work; otherwise, minima may be found in almost any region of the scale. When minima have been located for a compound of a series, the direction in which the trolley must be moved in order to locate minima for other compounds of the series may be predicted.

After water was obtained which was suitable for making solutions, the minima for salicylic acid were sought. When the water alone was used in the un-

* For previous articles in this series see J. CHEM. EDUC., **13**, 210–5; 276–81 (1936).

known cell and the scale was searched from −10.00 to +20.00, no minima were found which could not be accounted for. Water shows two minima at 9.24 and 9.30 which have resisted all efforts of removal. These two have been assigned to water. Another minimum at 16.10 is rarely absent, although it may be removed by distillation of the water in quartz. The minimum does not exist if pyrex-distilled water is observed immediately after distillation. However, since the position of this minimum is known, in ordinary work one need not attempt to remove it; in fact, it serves as a reference minimum for checking calibration and for determining whether an observer is reading minima. A solution of salicylic acid diluted to one part in 10^{11} parts of water was examined over this region and two minima at 6.09 and 6.19 were found in addition to those shown by water.

It was necessary, therefore, to determine whether the latter two minima belonged to salicylic acid or to an impurity introduced with the compound. Since a compound must be present in a concentration of approximately one part in 10^{12} of solvent to produce minima, it is evident that if the two minima observed in the aqueous solution of salicylic acid were those of an impurity it must have been present to the extent of ten per cent. The salicylic acid used was of high purity as indicated by its melting point; therefore, an impurity could not have existed to the extent of ten per cent. However, to avoid the possibility that the minima were the result of an impurity they were diluted out and then brought back by concentration. The 10^{11} solution was successively diluted with water, which had been shown to be free of the 6.09 and 6.19 minima, until the two minima were no longer visible. To this solution a small volume of the 10^{11} solution was added and the two minima returned. The actual concentration at which the minima could be made to appear and disappear was determined. Further, successive small portions of the 10^{11} solution were added to a known volume of pure water until the minima appeared. By repeated dilutions and concentrations it was established that the sensitivity of the apparatus to salicylic acid, or the concentration at which the 6.09 minimum became a threshold, was 7.1×10^{-13} g. of salicylic acid per ml., and that at which the 6.19 minimum became a threshold was 6.6×10^{-13} g. per ml. This method leaves no doubt that the minima observed were those of the compound used.

Benzoic acid and its substitution products, whose equivalent weights are lower than that of salicylic acid, will produce their minima at points lower on the scale than 6.09. After locating the minima for salicylic acid, those for benzoic acid, and mono methyl, amino, chloro, nitro, bromo, and iodo benzoic acids were located. Each pair of minima was identified as belonging to the compound in question in the same manner as in the case of salicylic acid.

METHODS OF QUANTITATIVE ANALYSIS

The magneto-optic apparatus may be operated quantitatively by two methods: (1) that of concentration[1] and (2) that of Nicol rotation[2] or the so-called circle method.

Concentration Method.—The apparatus will detect the presence of a compound even if its concentration is reduced to several parts in 10^{12} of water. There is a definite minimum concentration for each compound called its sensitivity, beyond which its minima cannot be observed. This minimum concentration is determined by successive dilutions of solutions of the pure compound. As a check on this value a measured volume of pure water is placed in the cell and successive small portions of a solution two orders higher in concentration than that of the first observed sensitivity are added from a micro-buret until the minima just appear. The two values usually do not differ more than a few tenths of a part in 10^{12}, and their average is taken as the true sensitivity. It should be noted that if the compound in question contains as much as ten per cent. of impurity, the minima caused by this would disappear long before those of the major constituent, and would reappear, on concentration, long after. In the concentration method one proceeds first to determine the sensitivity of the compound and then to ascertain the concentration of the sample at which the minima for the compound just appear. From these two values the percentage of the compound in the sample may be computed.

Nicol Rotation Method.—It has been found that minima can be read when the magnetic fields are assisting and the analyzing Nicol is rotated[3] in the direction of the magnetic rotation. Further study has shown that the angle of rotation of the analyzing Nicol from the uncrossed position necessary to cause the disappearance of the minima of a compound is a direct function of the concentration of the compound. The intensity of light is controlled by the use of a third Nicol placed just in front of the polarizing Nicol. The procedure in the Nicol rotation method is as follows: (1) preparation of a graded series of concentrations, *e. g.*, 10^{-3}, 10^{-5}, 10^{-7}, 10^{-9}, and 10^{-11} g. of the pure compound per g. of solution; (2) determination of the angle of rotation of the analyzing Nicol from the uncrossed position to cause a certain minimum of the compound to appear and disappear for each concentration; (3) plotting the logarithm of the reciprocal of the concentration against these angles (the curve which is obtained is almost a straight line in the region of very low concentrations); (4) determination in a known dilution of the unknown, of the angle of rotation of the analyzing Nicol from the uncrossed position to cause the minimum of the compound to appear and disappear; and (5) reading the concentration of the compound from the calibration curve. The angle of rotation is determined as follows. If the minimum is visible, the Nicol is rotated toward the crossed position in 5-degree increments until the minimum disappears. This is con-

[1] BISHOP AND DOLLINS, *J. Am. Chem. Soc.*, **54**, 4585 (1932).
[2] BISHOP, DOLLINS, AND OTTO, *ibid.*, **55**, 4365 (1933).
[3] ALLISON, CHRISTENSEN, AND WALDO, *Phys. Rev.*, **40**, 1052 (1932).

tinued until a 5-degree range is established over which the minimum can be made to appear and disappear. By careful rotation the range is narrowed to about 1 degree. The minimum is then turned in and out by rotating the Nicol by means of a fine adjustment and the average of the settings is taken as the correct angle. The angle can be reproduced to within 0.3 to 0.4 degree corresponding to errors of about 10 per cent. in concentration. In order to complete the curve it is necessary to determine the concentration of the compound for which the minimum will just appear when the analyzing Nicol is in the uncrossed position. To do this, small measured portions of a solution containing 1 part of the compound in 10^{10} parts of water are added to a known volume of pure water until observations, the Nicols being completely uncrossed, show the presence of the minimum as a threshold. This calculated threshold concentration is then plotted on the curve for zero angle.

Each observer must determine his own calibration curve for a compound which in most cases can be used for other compounds. He should spend considerable time in practice with the method before attempting to establish his calibration curve.

The method is more rapid than the concentration method but is possibly less accurate. It lends itself admirably to the tracing of changes in concentration during reactions involving the solvent. The concentration method, on the other hand, cannot be used in such instances.

CONCLUDING REMARKS

The operation of the magneto-optic apparatus is admittedly difficult and certain facts concerning its manipulation must be borne in mind. The extreme sensitivity of the apparatus makes essential the careful avoidance of all contaminations. The room in which the apparatus is situated should be darkened, and the operator should accustom his eyes to the darkness before attempting observations. Considerable time is consumed in acquiring the technic of keeping the apparatus in adjustment and an even longer time may be required in learning the reading of minima. Experience has shown that the reading eye of the observer is an important factor; some are unable to read minima even after repeated efforts, whereas others can make accurate settings almost immediately. Between these two extremes there are many eyes which, with continued practice, can make dependable observations. Anyone who contemplates the construction and use of the magneto-optic apparatus should see a set-up on which accurate minima are being observed in order to learn the technic of its operation. The physical characteristics of a minimum cannot be adequately described. A person who plans to begin this type of work should realize that many hours, weeks, and even months may be consumed before dependable observations can be made. Although the authors were able to read minima readily on Allison's two set-ups, they spent several months in actual practice before reliable observations could be made. Anyone who enters into this work with the preconceived idea that within a few weeks he will be obtaining positive results, adept though he may be at research, is almost certainly doomed to disappointment.

SOURCES *of* PICTURES

JEAN CUSHMAN, Assistant to the Editor

A NUMBER of our readers have written to the JOURNAL to ask for information on sources of alchemical pictures and of portraits of famous chemists. We are here offering a compilation of all the material we have been able to obtain on the subject, in the hope that it may serve as a convenient reference.

The compilation consists of three lists. The first is a list of companies or individuals from whom such pictures may be obtained, with information regarding sizes and prices. This list is alphabetical, and is numbered 1–8.

The second list in the compilation consists of sources from which portraits may be obtained but from which complete lists of chemical or alchemical subjects are not available. The reader is advised to communicate with one or more of these in case some particular portrait desired does not appear in our third list.

The third is a list of people whose portraits are available, with one or more numbers accompanying each name; these numbers correspond to those of the first list, thus showing where each portrait may be obtained. Two of the companies supplying portraits have given order numbers with the names of the subjects; these follow the list number in parentheses. For example: Bunsen: 1 (7-125E); 5; 6 (No. 2933); 7—means that a portrait of Bunsen may be purchased from the Central Scientific Company (where it is numbered 7-125E); from H. E. Kinsman; from Rudolf Lesch (where it is No. 2933); and from The Macmillan Company. The reader may then refer to the first list for detailed information about the portrait in which he is interested.

LIST OF SOURCES

1. Central Scientific Company, 1700 Irving Park Boulevard, Chicago, Illinois. The Harcourt Portraits—photographic reproductions of wood and steel engravings, drawings, paintings, and photographs, all from original sources. Ready for framing, each portrait as large as possible from contact reproduction from 8″ × 10″ plates; any twelve, $12.50; any six, $6.75; single portraits, $1.25. Prices include postage.

2. Gladwish & Mitchell, 1019 Dominion Square, Montreal, P. Q., Canada. Photographic copy of Stephenson's pencil sketch of John Dalton. Buff finish; 5″ × 7″, $0.25; 8″ × 10″, $1.00; 11″ × 14″, $2.00. Quotations will be made on other sizes upon request.

3. JOURNAL OF CHEMICAL EDUCATION, 20th and Northampton Streets, Easton, Pennsylvania. Two portfolios, each containing sixteen portraits which have previously appeared as frontispieces in the JOURNAL. These portfolios may be obtained at a price of $1.00 each. Series A contains portraits of Sir William Perkin, Robert Boyle, Frederick Wöhler, Svante Arrhenius, Madame Curie, M. Berthelot, Joseph Priestley, Louis Pasteur, H. Le Chatelier, Jacobus Henricus van't Hoff, Justus von Liebig, Adolf von Baeyer, Michael Faraday, Sir William Ramsay, Stanislao Cannizzaro, and Dmitri Mendeléeff. Series B contains portraits of F. W. Aston, R. W. Bunsen, J. M. Crafts, John Dalton, Emil Fischer, J. W. Gibbs, W. F. Hillebrand, Irving Langmuir, H. Moissan, W. Nernst, W. Ostwald, T. W. Richards, Benjamin Rush, P. Sabatier, Benjamin Silliman, Sr., and Benjamin Thompson, Count Rumford. These portraits are printed on a heavy glossy paper, and are suitable for framing; each is accompanied by a short biographical sketch of the subject.

4. D. H. Killeffer's "Portraits and Sketches of Eminent American Chemists." Order through Mr. George Bittner, c/o The Chemical Catalog Co., 330 West 42nd Street, New York City. Sizes 8″ × 10″, suitable for framing. Biographical sketch of each subject printed on separate sheet. Complete set, 28 subjects, postpaid, $3.00.

5. H. E. Kinsman, 38 Spring Street, Williamstown, Massachusetts. Copies from photographs and from cuts in books or pamphlets, mostly 3″ × 4″ and 4″ × 6″. Furnished in either dull or glossy finish, unmounted; size 4″ × 6″, $0.50 per print; 8″ × 10″, $1.00 per print; 16″ × 20″, for framing, $3.00. Could be furnished in other sizes if desired.

6. Rudolf Lesch Fine Arts Incorporated, 225 Fifth Avenue, New York City. Official agent for the Photographische Gesellschaft of Berlin. Portraits furnished in black-and-white photogravure, about 8″ × 10″, at $2.00 each.

7. The Macmillan Company, Advertising Department, 60 Fifth Avenue, New York City. Large steel and photogravure portraits in varying sizes, $2.00 each.

8. Science Service, Twenty-first and Constitution Avenue, Washington, D. C. Large collection of portraits of scientific men; dull or glossy finish; sizes and prices: 4″ × 5″, $0.35; 5″ × 7″, $0.50; 6″ × 8″, $0.75; 8″ × 10″, $1.00; 10″ × 12″, $2.00; 12″ × 16″, $3.00. These prices do not include publication rights. Remittance must be sent with order. Science Service does not issue a printed list of the portrait photographs in its files, nor does it have any separate list of chemists, but it probably does have more portraits of chemists in its files than are included in the "List of Portraits" which follows. Anyone desiring a portrait which he does not find in this list might communicate directly with Science Service for further information.

SUPPLEMENTARY LIST OF SOURCES

The Berolzheimer Series of Alchemical and Historical Reproductions. These prints of famous paintings appear throughout the 1931–36 volumes of *Industrial and Engineering Chemistry*. Detailed instructions for obtaining photographic copies of the prints appear on page 129 of the January, 1936, issue of *Industrial and Engineering Chemistry;* also on that page appears a list of all the prints of the series published to that date.

The New York Public Library, Fifth Avenue and Forty-second Street, New York City, has an Art Division scrapbook entitled "Medicine and Related Subjects" which contains approximately fifty illustrations of alchemical subjects. The subject index of paintings kept in the Division lists twenty-five reproductions of paintings on the subject. Both scrapbook and index receive additions more or less constantly. Any of this material may be photostated.

The Nobel Prize portraits. Nobelstiftelsen, Stockholm, Sweden. The Nobel Foundation has a complete collection of portraits of all the Nobel Prize winners. A limited number of copies are for sale from the Foundation; in general, they are about 10 × 14 cm., and the price is 1 Swedish crown each. Portraits of prize winners from 1920 on may be used for reproduction only after permission has been obtained from the photographer; the name of the photographer must be obtained from the prize winner.

Portraits of contemporary scientists may often be obtained from the various photographic news agencies, such as Underwood & Underwood, Wide World Photos, and Keystone Views. These come in gloss-finish prints, about 8″ × 10″; the usual price is $3.00, although they sometimes run as high as $5.00. In writing to such an agency it is necessary to specify the portraits desired; the agency would not be able to supply, for example, a list of chemists, as their portraits are not so classified.

Julian P. Scott's Kodak Pictures of Chemists and Pharmacologists. Chiefly portraits of contemporary scientists, sold by W. F. Roberts Co., 829 17th Street, Washington, D. C. In post-card size, they are $0.20 each; 7″ × 11″ enlargements are $1.00 each.

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ELEMENTS *of the* QUANTUM THEORY*

SAUL DUSHMAN

Research Laboratory, General Electric Co., Schenectady, New York

CHAPTER X. THE HYDROGEN MOLECULE. PART II. THE VARIATIONAL METHOD

METHOD OF SECULAR EQUATION

WHILE the HL method yields only an approximate value for the energy of formation of H_2 from the atoms, more accurate results have been obtained in the solution of this problem as in that of the helium atom, by the application of the variational method. As a first illustration of this, it is interesting to observe how much more readily the eigenvalues may be derived in this manner as compared with the rather tedious calculation by HL in which the perturbation method was used.

As shown in Chapter IX, Part II, we can write the condition for the solution of the S. equation in the form

$$E = \frac{\int \phi H \phi d\tau}{\int \phi^2 d\tau} = \text{minimum} \tag{361}$$

where H is defined by equation (412).

Let us assume, as in the first part of this chapter that the zero-order eigenfunction, ϕ^0, is a linear combination of the functions

$$\phi_1 = u_A(1)u_B(2) \tag{401}$$

and

$$\phi_2 = u_A(2)u_B(1) \tag{403}$$

where $u_A^{\sim}(1)$, etc., are of the form shown in equation (402).

Let

$$\phi^0 = a\phi_1 + b\phi_2 \tag{449}$$

Since ϕ_1 and ϕ_2 are orthonormalized functions, it follows from (448) that

$$(a^2 + b^2 + 2abS^2)E = a^2H_{11} + ab(H_{12} + H_{21}) + b^2H_{22} \tag{450}$$

where

$$\left.\begin{aligned} H_{11} &= \int \phi_1 H \phi_1 d\tau \\ H_{12} &= \int \phi_1 H \phi_2 d\tau \\ H_{21} &= \int \phi_2 H \phi_1 d\tau \\ H_{22} &= \int \phi_2 H \phi_2 d\tau \end{aligned}\right\} \tag{451}$$

Because of the equivalence of the two electrons, it is evident that

$$H_{11} = H_{22} \text{ and } H_{12} = H_{21}$$

Hence, equation (450) becomes

$$(a^2 + b^2 + 2abS^2)E = (a^2 + b^2)H_{11} + 2abH_{12}$$

Differentiating with respect to a and b, respectively, we derive two relations which must be satisfied. These are:

$$(a^2 + b^2 + 2abS^2)\frac{\partial E}{\partial a} = 2a(H_{11} - E) + 2b(H_{12} - S^2E) = 0,$$

$$(a^2 + b^2 + 2abS^2)\frac{\partial E}{\partial b} = 2a(H_{12} - S^2E) + 2b(H_{11} - E) = 0.$$

Consequently, we derive the determinantal relation

$$\begin{vmatrix} H_{11} - E, & H_{12} - S^2E \\ H_{12} - S^2E, & H_{11} - E \end{vmatrix} = 0,$$

that is, the secular equation,

$$(H_{11} - E)^2 - (H_{12} - S^2E)^2 = 0. \tag{452}$$

The roots of this equation are, evidently,

$$E_S = \frac{H_{11} + H_{12}}{1 + S^2} \tag{453}$$

and

$$E_A = \frac{H_{11} - H_{12}}{1 - S^2} \tag{454}$$

Utilizing equations (412) and (426), given in Part I,

$$\begin{aligned} H_{11} &= \int \phi_1^2(2E_0 + V_0 - V_1^B - V_2^A)dv_1dv_2 \\ &= 2E_0 + \frac{e^2}{R} + e^2\int (1/r_{12})\phi_1^2 dv_1dv_2 \\ &\quad - e^2\int\left(\frac{1}{r_{B1}} + \frac{1}{r_{A2}}\right)\phi_1^2 dv_1dv_2 \\ &= 2E_0 + \frac{e^2}{R} + J_1 - 2J_2 \end{aligned} \tag{455}$$

where J_1 and J_2 are expressions defined by equations (441) and (442), respectively. Comparing with equation (444), it is seen that

$$H_{11} = 2E_0 + E_{11} \tag{456}$$

In the same manner it is shown that

$$\begin{aligned} H_{12} &= \int \phi_1\phi_2\{2E_0 + V_0 - V_1^A - V_2^B\}dv_1dv_2 \\ &= S^2\left(2E_0 + \frac{e^2}{R}\right) + e^2\int (1/r_{12})\phi_1\phi_2 dv_1dv_2 \end{aligned}$$

* This is the fourteenth of a series of articles presenting a more detailed and extended treatment of the subject matter covered in Dr. Dushman's contribution to the symposium on Modernizing the Course in General Chemistry conducted by the Division of Chemical Education at the eighty-eighth meeting of the American Chemical Society, Cleveland, Ohio, September 12, 1934. The author reserves the right to publication in book form.

$$-e^2\int\left(\frac{1}{r_{A1}}+\frac{1}{r_{B2}}\right)\phi_1\phi_2 dv_1 dv_2$$
$$= S^2\left(2E_0+\frac{e^2}{R}\right)+K_1-2SK_2 \qquad (457)$$

where K_2 and K_1 are the expressions defined by equation (445) and (446), respectively. Comparing with equation (447), it follows that

$$H_{12} = 2E_0S^2 + E_{12} \qquad (458)$$

Hence

$$E_S - 2E_0 = \frac{E_{11}+E_{12}}{1+S^2} = \eta_\alpha \text{ [see equation (432)]}$$
$$= \frac{e^2}{R}+\frac{J_1-2J_2+K_1-2SK_2}{1+S^2} \qquad (459)$$

while

$$E_A - 2E_0 = \frac{E_{11}-E_{12}}{1-S^2} = \eta_\beta \text{ [see equation (435)]}$$
$$= \frac{e^2}{R}+\frac{J_1-2J_2-K_1+2SK_2}{1-S^2} \qquad (460)$$

These results are identical with those derived in equations (443) and (447).

METHOD OF MOLECULAR ORBITALS

In the HL method the eigenfunctions for the H_2 molecule are obtained as linear combinations of functions which are products of *atomic orbitals*, that is, one-electron wave functions which describe the motion of an electron in the field of only one atom. On the other hand, F. Hund, R. S. Mulliken,[1] and others have investigated the possibilities of developing wave functions which shall express the motion of each electron in the potential field resulting from all the nuclei and other electrons present in the molecule. Thus, in this method the system H_2 is regarded as the result of the addition of an electron to the ion H_2^+. The point of view is therefore analogous to that of Hartree in the case of atomic systems.

A comparison of the results obtained by the two methods has been made by Van Vleck and Sherman and their conclusion is as follows:[2]

"It is hard to say categorically whether the method of molecular orbitals or the HL method is the better. The latter undoubtedly is much preferable at very large distances of separation of the atoms, for then the continual transfer of electronic charge from one atom to another demanded by the ionic terms surely scarcely occurs at all. On the other hand, at small distances, the HL method probably represents excessive fear of the r_{12} effect, and the factorization into n one-electron problems presupposed by the method of molecular orbitals may be quite a good approximation."

The reference to "ionic terms" requires further amplification, and, in order to illustrate the significance of this point, we shall consider the application of the two methods to a diatomic molecule AB in which each atom contains only one electron which is effective for interaction.

In the molecular orbital method, we represent the eigenfunction for the molecule by

$$\Psi = \psi_1(x_1y_1z_1)\cdot\psi_2(x_2y_2z_2) \qquad (461)$$

where a capital Ψ is used, as Van Vleck and Sherman have suggested, to denote the wave function for the whole system, and small ψ for the function of each electron moving in the field of the two nuclei and the other electron.

Let ϕ_A denote the wave function for the motion of one electron in the field of the nucleus A (so that ϕ_A is an atomic orbital), and similarly for ϕ_B.

Then equation (461) becomes,

$$\Psi = [\alpha\phi_A(1)+\beta\phi_B(1)][\alpha\phi_A(2)+\beta\phi_B(2)]$$
$$= \alpha^2\phi_A(1)\phi_A(2)+\beta^2\phi_B(1)\phi_B(2)$$
$$+\alpha\beta[\phi_A(1)\phi_B(2)+\phi_A(2)\phi_B(1)]. \qquad (462)$$

It will be noted that a term such as $\phi_A(1)\phi_A(2)$ implies that both electrons are associated with nucleus A, while $\phi_B(1)\phi_B(2)$ means that both electrons are associated with B. Therefore, the right-hand side of (462) represents a condition which may be described as follows:

(1) The system has a probability of being in either or both (depending upon the ratio α/β) of the *ionic states* $A^-:B^+$, or $A^+:B^-$.

(2) There is a probability, defined by $\alpha^2\beta^2$, that the molecule will exist in the *homopolar* state A : B, in which the bond is *non-polar*.

The HL argument takes into account only the second possibility and neglects completely the possible occurrence of ionic states.

Obviously the actual wave function should, in general, be represented by a combination of ionic and homopolar functions, and for purposes of further discussion, we may write equation (462) in the more compact form,

$$\Psi = a\psi_i + c\psi_{HL} \qquad (463)$$

where ψ_i designates the wave function for the ionic states, ψ_{HL} that for the homopolar state (HL form of function), and it is necessary that

$$a^2 + c^2 = 1.$$

From this point of view, the distinction between ionic and homopolar compounds is not nearly so sharp as we ordinarily assume. As a in equation (463) varies from 1 to 0, we pass from the completely ionic to completely homopolar type of molecule. In this connection the comments of Van Vleck and Sherman are very pertinent.

"There are elements of truth," they write, "in the old-fashioned chemistry that HCl has the structure H^+Cl^-, as the true wave function of HCl is expressible as a linear combination of various idealized types, and certainly H^+Cl^- must be given some representation.... One great service of quantum mechanics is to

[1] R. S. MULLIKEN, *Rev. Mod. Phys.*, **4**, 1 (1932). See also J. H. VAN VLECK AND A. SHERMAN, *ibid.*, **7**, 168 (1935) for a comprehensive discussion of this topic and bibliography.

[2] VAN VLECK AND SHERMAN, *loc. cit.*, p. 171.

show very explicitly that *all gradations of polarity are possible*, so that in a certain sense it is meaningless to talk of such *idealizations* as homopolar bond, heteropolar bond, covalent bond, dative bond, etc."[3]

The reader will find further interesting remarks on this topic in Pauling's paper,[4] "The transition from one extreme bond type to another," in which he uses as illustrations of such transitions from ionic to homopolar molecules the alkali and hydrogen halides.

THE DISSOCIATION ENERGY OF H_2

These considerations have been found to be important in the calculation of the energy of formation of H_2 from the atoms. (This will be designated by D_e.) For a symmetrical molecule, such as H_2, we usually regard the value of a in equation (463) as insignificant. However, S. Weinbaum[5] has shown that it is possible, by using a function of the form given in equation (463), to obtain a more accurate value of D_e. He assumed

$$\Psi = [\phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2)] + c[\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)] \quad (464)$$

$$\phi_A(1) = \sqrt{\frac{Z^3}{\pi}}\,\epsilon^{-Zr_{A1}}$$

and similar expressions for the other hydrogen-like functions. This expression for Ψ was then used in the fundamental relation (361) to calculate a value of E, subject to the conditions, $\frac{\partial E}{\partial c} = 0$ and $\frac{\partial E}{\partial Z} = 0$.

The lowest value for D_e obtained in this manner was 4.00 v.e., with the values $c = 0.256$ and the effective nuclear charge $Z = 1.193$.

E. A. Hylleraas[6] also used the method of molecular orbitals, starting with wave functions which were solutions for ionized hydrogen molecule, H_2^+. The value thus derived for D_e was 3.6 v.e.

Passing now to the consideration of other variational treatments in which atomic orbitals have been used, we find that S. C. Wang[7] used modified HL function of the form

$$\Psi = C\{\epsilon^{Z(r_{A1} + r_{B2})} + \epsilon^{Z(r_{A2} + r_{B1})}\} \quad (465)$$

where C is a normalization constant, and Z, as before, represents an effective nuclear charge which was determined by solving equation (361), subject to the condition $\partial E/\partial Z = 0$.

A more elaborate expression for Ψ was utilized by N. Rosen.[8] He took into account the distortion in the charge distribution in each atom which must occur when the two atoms are brought together (the polarization effect).

"The simplest way," he writes, "to represent this distortion is to consider the radius of the atom to change with the distance from the other atom. This is effectively what Wang did in his calculations, and it led to a definite improvement in the energy value. However, since the perturbations involved are not spherically symmetrical this cannot be a very good approximation to the true state of affairs, and the next improvement that suggests itself is to introduce a change in the wave function that will depend on the direction with respect to the molecular axis and will be greatest in the direction of the latter. Since the interactions can be thought of roughly as being along this axis, it seems likely that the electron cloud tends to bulge out in the direction of the second atom."

In accordance with this idea, Rosen used a modification of Wang's "trial function," as defined in equation (465) of the form,

$$\Psi = C[\epsilon^{-\alpha(r_{A1} + r_{B2})}(1 + \beta r_{A1}\cos\theta_{A1})(1 + \beta r_{B2}\cos\theta_{B2}) + \epsilon^{-\alpha(r_{B1} + r_{A2})}(1 + \beta r_{B1}\cos\theta_{B1})(1 + \beta r_{A2}\cos\theta_{A2})] \quad (466)$$

where θ_{A1} is the angle between r_{A1} and R (the line joining the nuclei), β is a variable parameter, and C is the normalization constant. Substituting this function in the variation equation (361), the effect was first determined of varying the effective nuclear charge α, assuming $\beta = 0$. The value of α thus obtained which corresponded to a minimum value of E was then substituted in equation (466) and used to calculate a minimum value of E for variations in β. The final result led to a value for D_e of 4.02 v.e., with the corresponding values of the two parameters, $\alpha = 1.19$, and $\beta = 0.10$ for the equilibrium distance, $R = 1.416\,a_0$.

The most accurate value for D_e has been calculated by H. M. James and A. S. Coolidge.[9] They used a separate set of elliptic coördinates (λ_1, μ_1 and λ_2, μ_2) for each electron and introduced a new coördinate $\rho = 2r_{12}/R$, thus taking into account a factor which had been neglected (because of mathematical difficulties) by previous investigators. As trial function they used the series

$$\Psi = \Sigma C[mnjkp]$$

where

$$[mnjkp] = \frac{1\epsilon}{2\pi}^{-\delta(\lambda_1 + \lambda_2)}(\lambda_1^m\lambda_2^n\mu_1^j\mu_2^k\rho^p + \lambda_1^n\lambda_2^m\mu_1^k\mu_2^j\rho^p)$$

and the summation extends over positive value of the exponents (including zero), "subject to the restriction required by nuclear symmetry that $j + k$ must be even, and taking as many terms as shall prove necessary give an acceptable approximation for the energy."

It was found that with $R = 1.40a_0$ and $\delta = 0.75$, five terms in the series were sufficient to give a value for E much better than any previously obtained. Actually, calculations were carried out with as many as 13 terms in the series. Table 1 taken from their paper gives a comparison between their results and those of previous investigators.

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[3] VAN VLECK AND SHERMAN, *loc. cit.*, p. 171. The author is responsible for the italicized parts.

[4] PAULING, *J. Am. Chem. Soc.*, **54**, 988 (1932). See also the discussion by L. PAULING AND J. B. WILSON, JR., "Introduction to quantum mechanics," p. 345.

[5] S. WEINBAUM, *J. Chem. Phys.*, **1**, 593 (1933).

[6] E. A. HYLLERAAS, *Z. Physik*, **71**, 741 (1931).

[7] S. C. WANG, *Phys. Rev.*, **31**, 579 (1928).

[8] N. ROSEN, *ibid.*, **38**, 2099 (1931).

[9] H. M. JAMES AND A. S. COOLIDGE, *J. Chem. Phys.*, **1**, 825 (1933).

TABLE 1

Function	D_e *(electr on-volts)*	R/a_0
One term	2.56	1.40
5 terms	4.504	1.40
11 terms	4.685	1.40
13 terms	4.698	1.40
Without r_{12}	4.27	1.40
Heitler-London	2.9	1.40
Sugiura	3.2	1.51
Wang	3.76	1.42
Rosen	4.02	1.416
Observed	4.72	1.40

It is of interest to compare these calculated values of D_e with the results of observations on the energy of dissociation of H_2, which we shall designate by D_0. Direct thermochemical determination by F. R. Bichowsky and L. C. Copeland[10] gave the value $D_0 = 4.55 \pm 0.15$ v.e., while H. Beutler[11] has deduced from the observations on the vibrational energy levels of H_2 in the normal state, the value $D_0 = 4.45$ (= 102,480 cal.). Since the energy minimum ($-D_e$) as calculated by the methods of quantum mechanics includes the zero-point energy ($^1/_2h\nu_0 = 0.27$ v.e., as shown in the following section), the observed value of D_e is $4.45 + 0.27 = 4.72$ v.e., which is in extremely satisfactory agreement with that deduced by James and Coolidge.

*PART III. VIBRATIONAL AND ROTATIONAL STATES OF THE HYDROGEN MOLECULE**

GENERAL REMARKS

The existence of band spectra, and the observations on the variation in specific heats of gases with temperature, lead to the conclusion that, in addition to the energy of excitation of electronic levels, the molecules also possess both vibrational and rotational energy due to the motions of the nuclei. Since the frequencies of these motions are small compared to those of the electrons, the electronic motion can adjust itself relatively instantaneously to the motion of the nuclei as if the latter were centers of force at rest.

It is therefore possible to consider the energy states arising from nuclear motions as superimposed upon the electronic states.

Let us consider a diatomic molecule, such as H_2. As shown in Part I, the potential energy for any two atoms, A and B, which combine to form a molecule AB, is a function of the internuclear distance, r, which may be represented graphically by a curve such as that shown in Figure 57. Let $U(r)$ designate this function. By definition the force between the nuclei is given by

$$F(r) = -dU/dr$$

At the value of $r = r_0$, for which U is a minimum, the force vanishes, while it is negative to the right of the minimum (corresponding to a net force of attraction) and positive to the left of the minimum (corresponding to a net force of repulsion).† If we assume $U(r) = 0$ for $r = \infty$, then the energy at $r = r_0$ (which is negative) corresponds to the dissociation energy which is usually designated by $-D$.

For values of $U(r) > -D$, there are two values of r at which $U(r)$ has the same value. These correspond to mean points of equilibrium for the vibrational motion of the nuclei, and the total energy is given by $E_v = U(r) + D$. This energy is quantized so that there exist a series of vibrational energy states, designated by the quantum numbers $v = 0, 1, 2, 3$, etc. between the values $U(r) = -D$ and $U(r) = 0$. Figure 57 shows such a series of vibrational energy states for the molecule H_2 in the normal ($1s'\Sigma_g^+$) state, and the potential energy curve derived in accordance with Morse's equation, as explained in the following section.

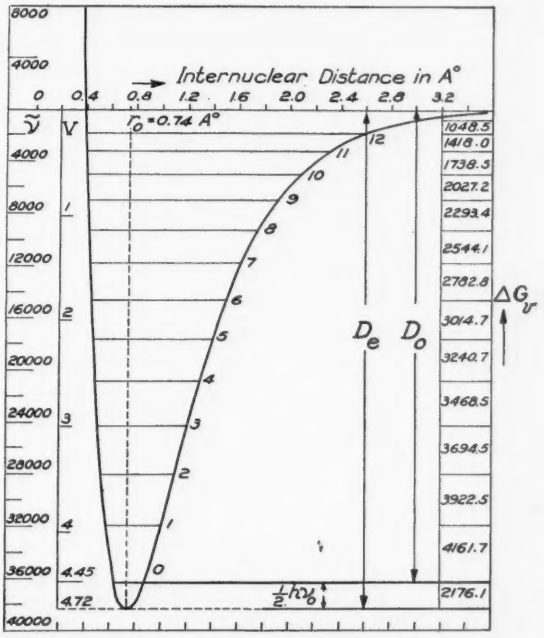

FIGURE 57.—POTENTIAL ENERGY FUNCTION AND VIBRATIONAL ENERGY LEVELS FOR NORMAL STATE OF H_2 MOLECULE

It is also observed that with any given vibrational state there are associated a series of rotational energy states, designated by the quantum numbers $K = 0$, 1, 2, etc. Thus, any line in the emission spectrum of a molecule may be represented as a transition from an

* The most recent discussion of the topic of band spectra is a publication of H. SPONER, "Molekülspektren und ihre Anwendung auf chemische Probleme," two volumes, Julius Springer, Berlin, **1936.**

† See also remarks at the beginning of Chapter VII, J. CHEM. EDUC., **12,** 581 (1935).

[10] F. R. BICHOWSKY AND L. C. COPELAND, *J. Am. Chem. Soc.*, **50,** 1315 (1928).

[11] H. BEUTLER, *Z. physikal. Chem.*, **B29,** 315 (1935).

upper rotational level K' associated with the upper vibration level v' and with a higher electronic state to a lower rotational level K'', which is associated with a vibrational level v'' and a lower electronic state. That is, if $\tilde{\nu}$ represents the wave-number* of the emitted line,

$$\tilde{\nu} = \tilde{\nu}_e + G_v' - G_v'' + F'(v, K) - F''(v, K) \qquad (467)$$

where $\tilde{\nu}_e$ denotes the wave-number difference between the lowest levels associated with $v' = v'' = 0$ and $K' = K'' = 0$, G_v' corresponds to the vibrational energy, and $F'(v, K)$ to the rotational energy associated with the higher electronic state and similarly for G_v'' and $F''(v, K)$.

Thus Figure 58 shows the lower vibrational energy levels for the molecule H_2 in the normal ($1s'\Sigma_g^+$) and in the first excited ($2p'\Sigma_u^+$) states.† The latter state results from the interaction of one electron in the normal ($1s$) state and another in the $2s$-state. The difference in energy for the states $v = 0$, $K = 0$ is equal to 90,201 cm.$^{-1}$ (= 11.13 v.e.) and the spectrum emitted by transitions from the higher to the normal state lies in the ultra-violet region, as shown by the values of λ (in Ångstroms) which are attached to the different lines.

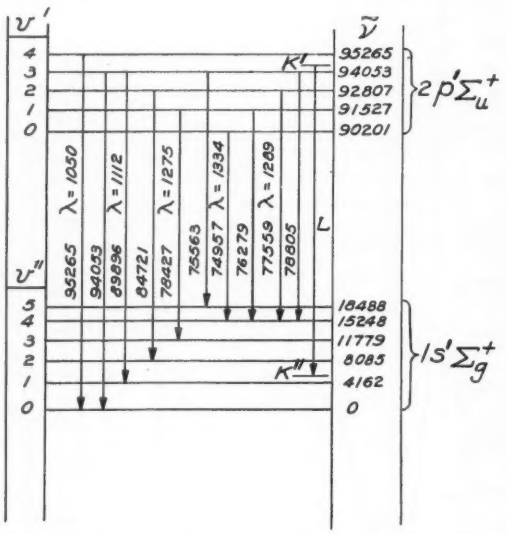

FIGURE 58.—NORMAL AND FIRST EXCITED ELECTRONIC ENERGY LEVELS FOR H_2 MOLECULE AND ASSOCIATED VIBRATIONAL ENERGY LEVELS

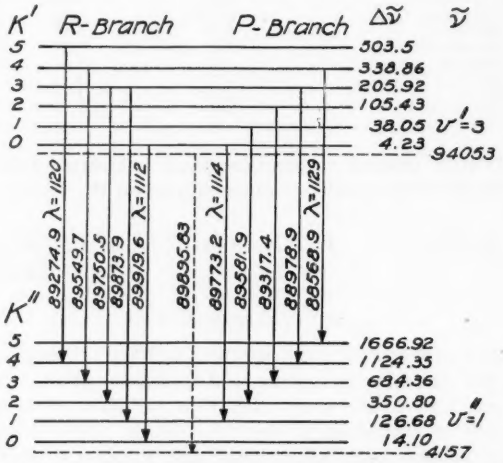

FIGURE 59.—ILLUSTRATING TRANSITIONS BETWEEN ROTATIONAL ENERGY LEVELS ASSOCIATED WITH TWO DIFFERENT VIBRATIONAL ENERGY LEVELS FOR H_2 MOLECULE

Figure 59 shows the rotational energy levels associated with the level, $v' = 3$, in the upper electronic state and the level, $v'' = 1$, in the normal state of the H_2 molecule. The values of $\tilde{\nu}$ on the right-hand side are taken from the corresponding values in Figure 58,‡ while the values under $\Delta\tilde{\nu}$ give the total increase in rotational energy (in terms of wave-numbers) as the quantum number K is increased from 0 to higher values. The transitions indicated are those corresponding to the line L in Figure 58, where K' designates the upper levels and K'', the lower levels, respectively. It will be seen that the "head" of the band, corresponding to the transition from $K' = 0$ to $K'' = 0$, has the value $\tilde{\nu} = 89896$ (or $\lambda = 1112$ Å). This is shown in Figure 58 as the third line from the left.

VIBRATIONAL ENERGY STATES

For the H_2 molecule in the normal state, the equilibrium internuclear distance, as shown in the previous sections, is $r_0 = 0.74$ Å. As the molecule acquires increasing amounts of vibrational energy (due to increase in temperature of the gas), this internuclear distance increases. Assuming that the restoring force acting on each atom in a diatomic molecule, AB, is proportional to the displacement from the position of equilibrium for minimum value of $U(r)$ (Hooke's law), it is possible to derive relations for both the potential energy as a function of r and the frequency of vibration.[12]

* $\tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda}$, where c = velocity of light, and λ = wave-length. It is customary to give energy differences in terms of wave-numbers. For the purpose of converting to other units of energy, the following relations are useful. (See R. T. BIRGE, *Phys. Rev. Supplement*, **1**, 1 (1929) for values of physical constants.)

1 electron volt (v.e.) = 8106 cm.$^{-1}$
= 23,055 cal./mole
= 1.591×10^{-12} ergs.
cm.$^{-1}$ = 2.844 cal./mole

† The values of the energy levels for H_2 indicated in this and the other figures are taken from the extremely interesting paper by C. R. JEPPESON, *Phys. Rev.*, **44**, 165 (1933) on "The emission spectrum of molecular hydrogen in the extreme ultraviolet."

‡ The difference between the values 4162 and 4157 for $\tilde{\nu}_0$ of the level $v'' = 1$ is of no significance.

[12] R. DE L. KRONIG, "The optical basis of the theory of valency," p. 83, published by The Macmillan Company, New York, **1935**. The reader will find this treatise extremely valuable in connection with the discussion on band spectra and their significance in relation to chemical properties.

We shall consider the general case of a diatomic molecule consisting of atoms A and B. Let μ_A and μ_B denote the masses of the atoms; let r denote the distance between the two nuclei for any given vibrational state, and let r_0 designate the value of r for $U(r) = -D$.

Then, the equations of motion for the two nuclei are as follows (see Figure 60):

$$\mu_A \ddot{x}_1 = k(r - r_0) = -k(x_1 - x_2)$$
$$\mu_B \ddot{x}_2 = -k(r - r_0) = k(x_1 - x_2).$$

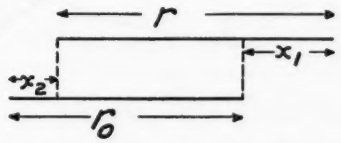

FIGURE 60.—ILLUSTRATING THE VIBRATIONAL MOTION OF TWO NUCLEI

Hence,

$$\ddot{x}_1 - \ddot{x}_2 = -k\left(\frac{1}{\mu_A} + \frac{1}{\mu_B}\right)(x_1 - x_2).$$

That is,

$$\ddot{r} = -\frac{k}{\mu}(r - r_0) \tag{468}$$

where $\mu = \dfrac{\mu_A \mu_B}{\mu_A + \mu_B}$ = "reduced" mass of molecule.

As shown in Chapter IV,[13] the solution of this equation is

$$r - r_0 = A \sin(2\pi\nu_0 t + \delta)$$

where A is the maximum amplitude, and

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{469}$$

The potential energy function corresponding to equation (468) is evidently a parabola with vertex at $r = r_0$, the equation for which is

$$U(r) = -D + \frac{k}{2}(r - r_0)^2$$

Substituting from equation (469), this can be written in the form

$$U(\rho) = -D + 2(\pi\omega_0)^2\mu\rho^2 \tag{470}$$

where $\rho = r - r_0$, and ν_0 is replaced by ω_0, in accordance with the notation used in the literature on band spectra.

This is the function which must be inserted in the S. equation for the system in order to determine the discrete energy states. This equation was deduced in Chapter VI,[14] and has the form

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dS}{d\rho}\right) - \frac{K(K+1)S}{\rho^2} + \alpha^2\{E - U(\rho)\}S = 0 \tag{471}$$

where $S = S(\rho)$ is the "radial" function, $K = 0, 1, 2,$ etc., and $\alpha^2 = 8\pi^2\mu/h^2$.

Put $S(\rho) = \dfrac{1}{\rho}\phi(\rho)$. Then equation (471) becomes,

$$\frac{d^2\phi}{d\rho^2} - \frac{K(K+1)\phi}{\rho^2} + \alpha^2(E - U)\phi = 0 \tag{472}$$

If we substitute for $U(\rho)$ from equation (470), and let $K = 0$, that is, consider only the case in which there is *zero rotational energy*, and only vibrational energy, equation (472) becomes*

$$\frac{d^2\phi}{d\rho^2} + \alpha^2[E + D - 2(\pi\omega_0)^2\mu\rho^2]\phi = 0 \tag{473}$$

This equation is evidently similar to the equation for the linear harmonic oscillator,[15] and has as eigenvalues the series defined by the relation

$$E_v = -D + h\omega_0(v + 1/2), \tag{474}$$

where $v = 0, 1, 2,$ etc., corresponds to the vibrational quantum number.

It follows that the vibrational energy levels should be equally spaced. Actually, the distance between successive energy levels decreases, in the case of homopolar diatomic molecules, with increase in v. That is, the atoms do not behave as simple harmonic oscillators, and the motion is of the *anharmonic type*, with the result that to a first approximation, the vibrational energy must be represented by an expression of the form

$$E_v = -D + h\omega_0(v + 1/2) - hx\omega_0(v + 1/2)^2 \tag{475}$$

where x is a constant for any given molecule.

For $E = 0$, that is, when dissociation occurs, it is evident that $dE_v/dv = 0$. Consequently,

$$\omega_0 - 2x\omega_0(v + 1/2) = 0$$

that is, $(v + 1/2) = \dfrac{1}{2x}$,

and

$$D = \frac{h\omega_0}{2x} - \frac{hx\omega_0}{4x^2} = \frac{h\omega_0}{4x} \tag{476a}$$

or

$$\frac{D}{hc} = \frac{\omega_0^2}{4\omega_0 xc^2} \tag{476b}$$

This gives the dissociation energy in terms of wave numbers.

Hence, to a first approximation

$$E_v = -D + h\omega_0(v + 1/2) - \frac{h^2\omega_0^2}{4D}(v + 1/2)^2 \tag{477}$$

As shown by Morse, a potential energy function which is in agreement with this relation and with the

[13] J. CHEM. EDUC., **12**, 381 (1935).
[14] Equation (210), Chapter VI, *ibid.*, **12**, 531 (1935).

* The solution discussed in the following section is that given by P. M. MORSE, *Phys. Rev.*, **34**, 57 (1929); also in CONDON AND MORSE, "Quantum mechanics," Chapter V.
[15] J. CHEM. EDUC., **12**, 381 (1935), Chapter IV, equation (108*a*).

requirement that E_v shall be a minimum for $\rho = 0$ may be chosen of the form

$$U(\rho) = -2D\epsilon^{-\beta\rho} + D\epsilon^{-2\beta\rho} \qquad (478)$$

where β is obtained as follows.

For small values of ρ, the last equation becomes

$$U(\rho) = -D + \beta^2\rho^2 D.$$

This evidently has a minimum value, $U(\rho) = -D$ for $\rho = 0$, that is, the minimum occurs at $r = r_0$.

Comparing this with the equation (470) it follows that

$$\beta^2 D = 2\pi^2\mu\omega_0^2,$$

and substituting for D, from equation (476a)

$$\beta = \sqrt{\frac{8\pi^2 M\omega_0 x}{h}} = 0.2454\sqrt{M\omega_0 x} \qquad (479)$$

where

$$M = \mu \times 6.064 \times 10^{23},$$
$$= \text{mass in terms of oxygen} = 16.$$

Now C. R. Jeppeson[16] found that for values of the vibrational quantum number from $v = 0$ to $v = 11$, the difference in wave-numbers between successive levels is given by the relation,

$$\Delta G_v = 4417.19 - 262.63(v + {}^1/_2) + 9.34619(v + {}^1/_2)^2 - 0.76(v + {}^1/_2)^3 \qquad (480)$$

The values of ΔG_v thus calculated are shown in the column on the right-hand side of Figure 57. For $v = 1$, $\Delta G_v = 4161.70$, and it will be observed that the value of ΔG_v decreases with increase in v.

More recently H. Beutler[17] has been able to determine, from observations on the lines in the extreme ultraviolet spectrum, values of ΔG_v for $v = 12$, 13, and 14. If the values of ΔG_v are plotted as ordinates against $\sum_{v=0}^{v} \Delta G_v = \tilde{\nu}$, the total increase in wave-number from $v = 0$, to v, the resulting curve (see Figure 61) shows that $\Delta G_v = 0$ for $\tilde{\nu} = 36{,}100$ cm.$^{-1}$. Therefore, this value must correspond to the dissociation energy, D_0, of H_2 in the normal state. In terms of energy units,

$$D_0 = 36{,}100/8106 = 4.454 \text{ v.e.}$$
$$= 4.454 \times 23{,}055 = 102{,}680 \text{ cal./mole.}$$

From equation (480) it follows that for $v = -{}^1/_4$, $\Delta G_0 = 2176.1$. This therefore corresponds to the zero-point energy ($h\nu_0/2$), and must be added to D_0 to give D, the minimum value of the potential energy, $U(\rho)$. Thus, $D = 36{,}100 + 2176 = 38{,}276$ cm.$^{-1}$ = 108,800 cal./mole.

For H_2 ($M = 1.008$), the value of β according to equation (479) is 2.00. Hence the potential energy function for H_2, as derived from the spectroscopic vibrational energy levels is given, *in terms of wave-numbers*, by the relation

$$U(\rho) = 38{,}276(\epsilon^{-4\rho} - 2\epsilon^{-2\rho}) \qquad (481)$$

[16] C. R. JEPPESON, *loc. cit.*

[17] H. BEUTLER, *Z. physikal. Chem.*, **B27**, 287 (1934).

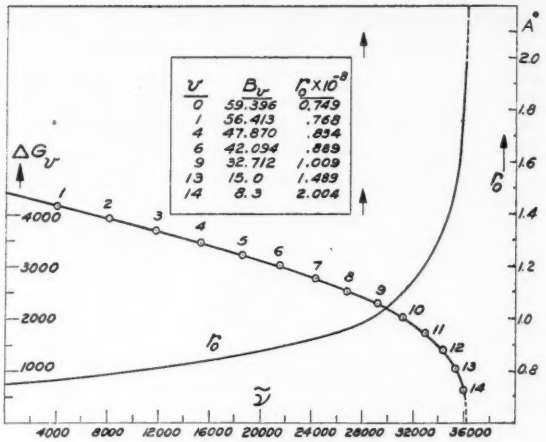

FIGURE 61.—PLOT OF ΔG_v AND INTERNUCLEAR DISTANCE (r_0) AS FUNCTIONS OF THE WAVE-NUMBERS OF THE VIBRATIONAL LEVELS FOR THE NORMAL STATE OF H_2

The following table gives values of $U(\rho)$ for different values of $r = \rho + 0.74$, in Ångstrom units.

r (Å.)	$U(\rho)$	r (Å.)	$U(\rho)$
0.34	+18,990	1.14	−26,650
0.44	−12,260	1.34	19,570
0.54	29,050	1.54	13,900
0.64	36,340	1.74	9,660
0.74	38,276	1.94	6,630
0.84	37,060	2.34	3,060
0.94	34,110	2.74	1,390
1.04	30,520	3.74	192

Figure 57 shows a plot of $U(\rho)$ versus r. The ordinates give the values of $U(\rho)$ both in terms of $\tilde{\nu}$, the wave-number, and in terms of V, the corresponding energy in electron volts. The horizontal lines give the vibrational energy levels corresponding to the different values $v = 0$ to $v = 12$, indicated on the curve. To distinguish D from D_0, the symbol D_e is customary for the former, which evidently has only a theoretical interest since D_0 *is the experimentally determined value.*

It will be observed that according to Jeppeson's data, $2x\omega_0 = 262.63$ while $\omega_0 = 2 \times 21{,}761$.

Hence, if we use Morse's relation,

$$D = \frac{(4352.2)^2}{525.26} = 36{,}060 \text{ cm.}^{-1}$$

which is less than the value determined by direct extrapolation to $\Delta G_v = 0$. As first shown by R. T. Birge and H. Sponer,[18] the latter method is the more accurate one for the determination of D_0.

A potential energy curve similar to that for the normal state can also be plotted for any of the excited states for which sufficient data on the vibrational energy levels are available. According to Jeppeson, the values of ΔG_v for the $2p'\Sigma_u^+$ state are given by the relation

[18] R. T. BIRGE AND H. SPONER, *Phys. Rev.*, **28**, 259 (1926).

$$\Delta G_v = 1357.302 - 39.9307(v + 1/2) + 1.218487(v + 1/2)^2 - 0.0638888(v + 1/2)^3$$

while the value corresponding to the zero-point energy is $\Delta G_0 = 673.7$ cm.$^{-1}$. Since the value of $2x\omega_0$ is 39.931, the calculated value of D_e is $\frac{(1347.4)^2}{79.862} = 22{,}860$ cm.$^{-1}$.

ROTATIONAL ENERGY LEVELS

Let us now consider the solution of equation (472) for the case $K \neq 0$. A solution of this equation has been given by C. L. Pekeris,[19] leading to an expression for the energy levels in which the effects of rotational and vibrational energies are combined. However, it is possible to indicate the significance of this more complicated expression without the formal mathematical derivation.

In Chapter V[20] it was shown that in the case of a rotating diatomic molecule with fixed moment of inertia, I, the rotational energy levels are given by the relation

$$E_r = \frac{h^2}{8\pi^2 I} K(K + 1) \qquad (482)$$

where K is the rotational quantum number, and I is derived by the relation

$$I = \mu r_0^2$$

where μ is the reduced mass.

Equation (482) is usually written in the form,

$$E_r = BK(K + 1) \qquad (483)$$

where

$$B = \frac{h^2}{8\pi^2 I}. \qquad (484)$$

In the case of H_2, $\mu_H = 1.662 \times 10^{-24}$ g. Therefore,

$$B_v = \frac{B}{hc} = \frac{3.32 \times 10^{-15}}{r_0^2} \text{cm.}^{-1}.$$

The notation B_v is used to indicate that the constant is measured in terms of wave-numbers and also that the value is a function of the vibrational quantum number.

According to equation (482), the levels should be equally spaced, if I were a constant; but, as in the case of the vibrational levels, not only does I vary with v, but also, for a given value of v, the spacing between rotational levels varies with change in K. Thus, in the case of H_2 and many other molecules, the value of ΔF, the increase in wave-number for $\Delta K = 1$, increases with increase in K, as is evident from Figure 59. Consequently, the actual observations on rotational energy levels lead to the semiempirical relation

$$\frac{E_r}{hc} = F = -\frac{1}{4} \cdot \frac{B}{hc} + \frac{B}{hc}(K + 1/2)^2 + \frac{A}{hc}(K + 1/2)^3 + \text{higher powers of } (K + 1/2). \qquad (485)$$

The first two terms on the right-hand side of this equation evidently correspond to the expression in equation (483), while the following terms are due to the effect of the vibrational energy. The expression deduced by Pekeris, which expresses the combined efforts of rotational and vibrational energy, is:[21]

$$\frac{E_{K,v}}{hc} = \omega_0(v + 1/2) - x\omega_0(v + 1/2)^2 + B_v K(K + 1) - \beta_0 K^2(K + 1)^2 - \gamma_0(v + 1/2)K(K + 1)$$

where

$$x = \frac{h\omega_0 c}{4D} \quad \text{.....See equation (476a)}$$

$$B_v = \frac{h}{8\pi^2 I c} \quad \text{.....See equation (484)}$$

and β_0 and γ_0 are constants, the values of which depend on those of r_0, ω_0, μ, and D.

Figure 59 shows the lower rotational levels associated with $v = 3$ for the electronic state $2p'\Sigma_u^+$ and similar levels associated with $v = 1$ for the normal state of H_2. The values under $\Delta\tilde{\nu}$ give the difference in wave-number of any given level with respect to the imaginary level designated by a dashed line, while $\tilde{\nu}$ gives the wave-number of this lowest level with respect to the level $\tilde{\nu} = 0$ for the normal H_2 molecule in state $v = 0$, $K = 0$. It will be observed that the differences between successive levels in both sets increase with increase in K, and that these differences for any pair of values of K' (the upper values) are less than for the corresponding pair in the set K'' (lower levels).

While it is possible to have transitions between any pair of vibrational levels, as shown in Figure 58, this is not valid for rotational levels. According to the selection principle for transitions, only those transitions may occur for which $\Delta K = \pm 1$. The lines corresponding to the transition from K' to $K'' = K' + 1$ constitute the P-branch, while those corresponding to the transition from K' to $K'' = K' - 1$ constitute the R-branch. In some cases, for reasons which we need not discuss here, lines are obtained for which $K'' = K'$. These then constitute the Q-branch.

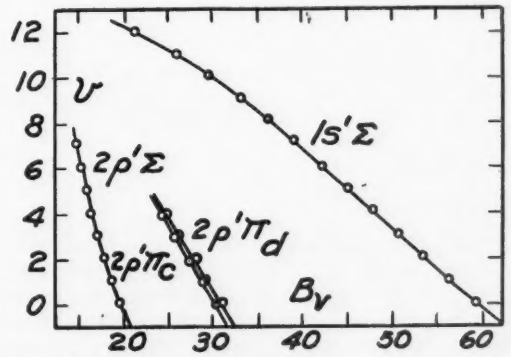

FIGURE 62.—PLOT OF B_v VERSUS v FOR THE NORMAL ($1s'\Sigma$) AND TWO EXCITED ELECTRONIC STATES OF H_2

[19] C. L. PEKERIS, *Phys. Rev.*, **45**, 98 (1934). See also L. PAULING AND E. B. WILSON, JR., "Introduction to quantum mechanics," Chapter X, for detailed discussion of this case.

[20] J. CHEM. EDUC., **12**, 436 (1935).

[21] L. PAULING AND E. B. WILSON, JR., *loc. cit.*, p. 274.

From equation (485) it is seen that the difference between the level $K = 0$ and the dashed level immediately below it, in Figure 59, is equal to $(1/4)B_v$. Hence for the state $v' = 1$, $B_v' = 4 \times 14.1 = 56.1$ cm.$^{-1}$, while for the level $v'' = 3$ in the upper electronic state, $B_v'' = 16.9$ cm.$^{-1}$. According to Jeppeson, the values of B_v for the different vibrational levels associated with the normal state are given by the relation

$$B_v = 60.8715 - 3.06709(v + 1/2) + 0.068393(v + 1/2)^2 - 0.0065(v + 1/2)^3$$

Figure 62, taken from the original publication, shows the variation in B_v with v for three different electronic states of the H_2 molecule.

It follows from equation (484) and these plots that *r increases with increases in v.* That is, as the vibrational energy increases, the atoms tend to vibrate about positions of equilibrium which are increasingly farther apart, and when dissociation occurs, B_v vanishes and r_0 becomes infinitely great. In Figure 61 there is shown a plot of r_0 versus $\tilde{\nu}$ which illustrates this conclusion graphically. It will be observed that while the value of r_0 for $v = 0$ is 0.75×10^{-8}, this increases with increase in v, and the rate of increase becomes greater as the stage of dissociation is approached, so that between $v = 13$ and $v = 14$, r_0 increases from 1.49 to 2.00×10^{-8} cm., and becomes infinite* between $v = 14$ and $v = 15$.

* The values of B_v for $v = 13$ and $v = 14$ are taken from the paper by H. BEUTLER, *loc. cit.*

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OTTO REINMUTH, Editor

CORRESPONDENCE

TITANIUM AND ITS MORE USEFUL COMPOUNDS

To the Editor

DEAR SIR:

A correction should be made in one paragraph of the article "Titanium and Its More Useful Compounds," appearing in the April issue. The statement is made, "TiO_2 has almost completely replaced ZnO in face powders. It is non-poisonous and enables greater permanent whiteness to be retained with the smallest amount of pigment, thus retaining the useful properties of the other ingredients."

The above statement was unfortunately worded and is not intended to indicate that zinc oxide has poisonous properties in face powders. Furthermore, the use of zinc oxide in this field is more extensive than that of TiO_2.

ROBERT M. MCKINNEY
WILLARD H. MADSON

KREBS PIGMENT & COLOR CORPORATION
WILMINGTON, DELAWARE

The TWELFTH CENSUS *of* GRADUATE RESEARCH STUDENTS *in* CHEMISTRY *and* CHEMICAL ENGINEERING, 1935

CALLIE HULL AND CLARENCE J. WEST

Research Information Service, National Research Council, Washington, D. C.

THE Twelfth Census of Graduate Research Students in Chemistry and Chemical Engineering (covering the academic year 1935–36) continues the annual compilations, the first of which was issued in 1924.* The present compilation includes returns from 142 universities, of which 18 have reported members of the faculty only engaged in chemical research.

The figures in the column headed Total in Table 2 refer to the graduate students only; *i. e.*, they do not include the figures for the faculty.

This year the figures indicate a gain over the previous year of 35 masters and a loss of only 2 in the number of doctors, as compared with an increase of 74 masters and 29 doctors for 1934. There is also reported a gain of 73 in the number of faculty members doing research against a reported increase of 113 last year. The only significant increases in particular fields are those in organic chemistry (increase of 74) and catalysis (increase of 22), while there is a decrease of 20 in industrial and engineering and of 46 in chemical engineering.

So many factors contribute to the reason for an increase or decrease in the number of students reported each year that it seems futile even to try to discuss them here.

The compilers wish to express their appreciation for the coöperation of the heads of the departments of chemistry of the institutions listed in Table 1, without which these statistics could not be assembled. The continued interest of the JOURNAL OF CHEMICAL EDUCATION in publishing the material is also acknowledged.

* ZANETTI, *Ind. Eng. Chem.*, **16**, 402 (1924); NORRIS, *ibid.*, **17**, 755 (1925); HULL AND WEST, J. CHEM. EDUC., **4**, 909 (July, 1927); **5**, 882 (July, 1928); **6**, 1338 (July-Aug., 1929); **7**, 1674 (July, 1930); **8**, 1374 (July, 1931); **9**, 1472 (Aug., 1932); **10**, 499 (Aug., 1933); **11**, 471 (Aug., 1934); **12**, 339 (July, 1935).

TABLE 2

NUMBER OF GRADUATE STUDENTS ENGAGED IN RESEARCH IN VARIOUS FIELDS OF CHEMISTRY AND CHEMICAL ENGINEERING

Subject	1935 *M*	1935 *D*	1935 *F*	1935 *Total*	1934 *Total*	1933 *Total*	1932 *Total*	1931 *Total*	1930 *Total*	1929 *Total*	1928 *Total*	1927 *Total*	1926 *Total*
General & Physical	171	331	283	502	498	522	595	577	520	448	406	430	343
Colloid	31	65	54	96	107	101	81	101	78	82	86	79	58
Catalysis	12	14	17	26	38	26	52	52	44	34	27	28	31
Subatomic & Radio	3	27	20	30	37	52	35	42	39	20	18	21	21
Electro-inorganic	14	23	9	37	36	51	51	55	49	24	25	21	32
Electro-organic	5	4	9	9	11	10	19	12	19	15	13	11	13
Photochemistry & Photography	11	39	28	50	57	52	57	43	44	41	22	25	25
Inorganic	71	79	73	150	147	138	162	159	129	116	124	116	109
Analytical	75	75	92	150	156	142	147	149	102	95	96	75	54
Metallurgical	43	26	38	69	55	47	74	78	46	36	22	21	34
Organic	374	570	334	944	870	862	943	930	811	719	668	570	475
Physiological	108	177	251	285	283	251	269	252	233	222	146	134	207
Pharmacological	4	10	32	14	15	14	15	13	16	14	11	7	14
Pharmaceutical	12	14	25	26	34	26	47	54	34	27	16	14	21
Sanitary	15	4	8	19	23	24	21	29	16	27	30	25	11
Nutrition	55	50	72	105	112	89	91	126	78	80	52	58	51
Food	33	15	24	48	34	49	35	32	34	31	52	27	37
Agricultural	72	67	86	139	133	129	161	126	108	91	111	89	72
Industrial & Engineering	74	28	52	102	82	66	82	84	63	91	156	183	274
Chemical Engineering	228	130	100	358	372	372	374	347	301	285	...	...	...
TOTALS	1411	1748	1607	3159	3126†	3023	3348‡	3261	2795**	2498	2081	1934	1882

† Includes 26 masters not classified.
‡ Includes 37 masters not classified.
** Includes 31 masters not classified.

TABLE 1—NUMBER OF GRADUATE STUDENTS ENGAGED IN RESEARCH IN
"M" indicates those working for a Master's degree, "D," Doctor's

Universities by States	General and Physical M D F	Colloid M D F	Catalysis M D F	Subatomic and Radio M D F	Electroinorganic M D F	Electroorganic M D F	Photochemistry and Photography M D F	Inorganic M D F	Analytical M D F	Metallurgical M D F	Organic M D F
Alabama:											
Ala. Poly. Inst.	1										3 2
Birmingham S. Coll.	1										1
Howard Coll.	1										1
U. of Ala.	1									1	1
Arizona:											
U. of Ariz.	2 1	1								2 1	2 2
Arkansas:											
U. of Ark.									1		2
California:											
Calif. Inst. Tech.	11 13						1 3 2	2 3 1	1		3 3
Claremont Colls.		1					2 1	1			1
Mills Coll.	1										1
U. of Southern Calif.	1	1		1				3	4 1 1		3 1 1
Stanford U.	3 5 5	2 4 4					2 7 2				8 3 5
Colorado:											
Colo. Coll.									1	1	1
U. of Colo.	3 2 1							2 1		1	1 3
Connecticut:											
Conn. State Coll.	1								1		2
Trinity Coll.	2 2		2 1					1	2		2 2
Wesleyan U.	1	1							1		27 18
Yale U.	1 19 9						2				1 1
Delaware:											
U. of Del.	1										
Dist. of Columbia:											
Am. U.	1							1	1 1	1	2 1
Catholic U.	3 1								3 1 1		4 2 2
Geo. Washington U.	1 1 1		1					1	1		1
Georgetown U.											
Florida:											
U. of Fla.	2							1	1 1		4 7 4
Georgia:											
Ga. Inst. Tech.	2						1		2		6
Hawaii:											
U. of Hawaii	1								1		3 1 2
Idaho:											
U. of Idaho	2 2	2 2						1	1		2 1
Illinois:											
Monmouth Coll.			1			1					7 13 5
Northwestern U.	1 4 5				1	1					23 61 17
U. of Chicago	13 18 6	4	2	7 4			3 4	10 7 3			5 27 5
U. of Ill.	2 15 3	5 1		1		1	1	3 6 3	3	2 1	
Indiana:											
De Pauw Univ.											1 2
Ind. U.	1 9 2	2 2	1 1		4 7 1		1	7 1 1	1 2 1		5 5 2
Purdue U.	3 6 3				1			1 2	1 4 1	5 2 2	7 14 4
U. of Notre Dame	4 1 1							1 1	5 1		12 11 5
Iowa:											
Grinnell Coll.	1										
Iowa State Coll.	5 3							1 2 2			1 24 1
State U. of Iowa	1 1 1	3 3 1	1 3			1	1	1 2	2 1 2	1 1 1	9 10 2
Kansas:											
Kan. State Agr. Coll.	1 2 5								1 1		2 3 2
Kan. U.	2 1						1	4 4 2	1 2	2	8 2 3
Kentucky:											
U. of Louisville	1				1						4 1
Louisiana:											
La. State U.	3 1							3 1			8 1 3
Sophie Newcomb C.											
Tulane U.	1	1						1			3 1
Maine:											
Bates Coll.											1
U. of Me.	2		1						1		2 2
Maryland:											
Johns Hopkins U.	5 7	3 3	1	4 3	1			1 2	2 1		12 7
U. of Md.	5 6 2							2 1 2	1		5 2
Massachusetts:											
Amherst Coll.			1 1						1		2 1
Boston Coll.								1 1			4 1
Boston Univ.					1			4 1			1 1 1
Harvard U.	19 16				6 1		3 3				25 14
Holy Cross Coll.	2										3
Mass. Coll. Pharm.											
Mass. Inst. Tech.	2 8 15							1 9 3			7 20 11
Mass. State Coll.	1 1							2	2 1		3 1
Mt. Holyoke Coll.	1 3									1	4 3
Tufts Coll.	1 2										1 1
Wellesley Coll.									1 1		1
Williams Coll.	1 1	1							1		1 1
Worcester Poly.	1		1								1 2
Michigan:											
Mich. State Coll.	3 4 2	1			1 1				3 1		4 2
U. of Mich.	6 1	7 1			4 1		2 1		6 4	11 9 4	16 5
Minnesota:											
U. of Minn.	1 16 3	2 9 2	1	6 2		1	1	2	4 4 3	1 5 1	6 30 5
Mississippi:											
U. of Miss.									1 1		5 1
Missouri:											
Mo. Sch. Mines	2							2 1	1	2	1
St. Louis U.	2 2			2 2				2 1	1		2 1 1
U. of Mo.	2 3 1	2 4							3 2 1		1 3 3
Washington U.	1 2 5		1	1	1	2	1 1				6 1 2

CHEMISTRY AND CHEMICAL ENGINEERING ACCORDING TO UNIVERSITY AND SUBJECT
degree, and "F," number of Faculty engaged in research.

Physiological M	D	F	*Pharmacological* M	D	F	*Pharmaceutical* M	D	F	*Sanitary* M	D	F	*Nutrition* M	D	F	*Foods* M	D	F	*Agricultural* M	D	F	*Industrial and Engineering* M	D	F	*Chemical Engineering* M	D	F	*TOTALS* M	D	F	*Universities by States*
																														Alabama:
					1																4						8		3	Ala. Poly. Inst.
																													2	Birmingham S. Coll.
																													2	Howard Coll.
		2			1									1							2			1			4		6	U. of Ala.
																														Arizona:
												2		2				1	2	3							9	2	10	U. of Ariz.
																														Arkansas:
		3							1		1			3	1		1			3	2						5		13	U. of Ark.
																														California:
		1			1																			6		2	10	20	23	Calif. Inst. Tech.
1																											4		3	Claremont Colls.
																											1		1	Mills Coll.
	6	3	2	2		1		3									1					1					10	13	13	U. of Southern Calif.
6	3	3													1	1	1										22	23	20	Stanford U.
																														Colorado:
																					1		1				3		2	Colo. Coll.
1	1	1				1	2		2		1																11	5	7	U. of Colo.
																														Connecticut:
		1																											5	Conn. State Coll.
																											4		3	Trinity Coll.
									1																		6		4	Wesleyan U.
	15	12																						1	7	2	2	68	44	Yale U.
																														Delaware:
																										1	1	1	2	U. of Del.
																														Dist. of Columbia:
																											2	4	2	Am. U.
																											7	6	4	Catholic U.
1	5	6																									3	6	10	Geo. Washington U.
	2	6																										2	6	Georgetown U.
																														Florida:
									3		1							3						1		2	12	8	10	U. of Fla.
																														Georgia:
																										4			15	Ga. Inst. Tech.
																														Hawaii:
1																		6		1							10	1	5	U. of Hawaii
																														Idaho:
																										1	6		8	U. of Idaho
																														Illinois:
																													2	Monmouth Coll.
5	3	5																									14	22	15	Northwestern U.
6	15	16			3			4			1	6	7	3	7	2	2			1		1					65	121	70	U. of Chicago
1	8	5							4	3														5	6	6	20	77	25	U. of Ill.
																														Indiana:
																											1		2	De Pauw Univ.
1	1																										23	28	7	Ind. U.
4	4	1				1	2						1					6	5	11	2		1				30	39	25	Purdue U.
																											22	12	8	U. of Notre Dame
																														Iowa:
																													1	Grinnell Coll.
	6	1										9	3	6	3	4	1	4	33	8				3	1	4	21	78	28	Iowa State Coll.
2	11	6			4			3		1	1	2	2	1	7	2	2							5	5	2	34	42	28	State U. of Iowa
																														Kansas:
5		3										8		4			1		2	3	1	1	1	2		2	19	9	22	Kan. State Agr. Coll.
																	1										15	6	12	Kan. U.
																														Kentucky:
2		2										1		1													7		6	U. of Louisville
																														Louisiana:
																		5	1	1	12	2	1	6		1	37	5	7	La. State U.
2		2																									2		2	Sophie Newcomb C.
	1	3															1										5	1	6	Tulane U.
																														Maine:
																													1	Bates Coll.
																		1		2							3		8	U. of Me.
																														Maryland:
4	1	4										2	10	5				4	1	3		2	1		5	2	6	44	35	Johns Hopkins U.
																											11	15	11	U. of Md.
																														Massachusetts:
					1																						3		3	Amherst Coll.
																											5		3	Boston Coll.
	1																										5	2	3	Boston Univ.
	3	11																										56	45	Harvard U.
																											5			Holy Cross Coll.
			1			2		2									1										3		2	Mass. Coll. Pharm.
																								55	21	10	65	58	40	Mass. Inst. Tech.
1	2	1												1													6	3	7	Mass. State Coll.
																											5		6	Mt. Holyoke Coll.
		2																				1					2		7	Tufts Coll.
1		1																									2		3	Wellesley Coll.
																											1		4	Williams Coll.
											1															1	3		5	Worcester Poly.
																														Michigan:
3	2	1																2									16	10	4	Mich. State Coll.
2	12	4		1	2							3	2	8										47	17	7	63	82	38	U. of Mich.
																														Minnesota:
4	13	6	1	1	4	3	5	2				1	2	2		1		7	3	1	5	1	2	7	3		43	99	37	U. of Minn.
																														Mississippi:
																		1		1	1		1				8		4	U. of Miss.
																														Missouri:
																										1	1	5	7	Mo. Sch. Mines
1	5	5																									3	11	9	St. Louis U.
3	5	4		1	2							5	5	4	1	2	1	4	6	7						1	22	30	30	U. of Mo.
1	5	6																			1					1	10	9	18	Washington U.

TABLE 1—(*Concluded*)

Universities by States	*General and Physical* M	D	F	*Colloid* M	D	F	*Catalysis* M	D	F	*Subatomic and Radio* M	D	F	*Electro-inorganic* M	D	F	*Electro-organic* M	D	F	*Photochemistry and Photography* M	D	F	*Inorganic* M	D	F	*Analytical* M	D	F	*Metallurgical* M	D	F	*Organic* M	D	F
Nebraska:																																	
U. of Neb.	5	2	4																				1								4	11	2
Nevada:																																	
U. of Nev.																							2										1
New Hampshire:																																	
Dartmouth Coll.																															3		1
U. of N. H.	2		2																							1					3		3
New Jersey:																																	
Princeton U.	5	1	7			1	2	1	2	1		4							1		2				4	2				3		6
Rutgers U.	3	3	1		1																				2	1				5	2	1
New Mexico:																																	
N. M. C. A. & M. A.																																	
New York:																																	
Albany Med. Coll.																																	
Columbia U.		27	19		5	3								1						3	1		2	4		7	4					29	19
Cornell U.	5	8	3							1		1										4	6	2		6	3				2	18	2
Fordham U.			1																								3				4	8	2
N. Y. S. Coll. For.																																	
N. Y. U.	5	5	2	1		1					6								3	5	2					1	1				15	10	5
Poly. Inst. Brooklyn	4		1											1								6		3	1	1					5	10	3
Rensselaer Poly.			1			1																	1						1		2	2	1
Syracuse U.	2	5	2	2		1																			3	4	1				4	2	1
Union Coll.			1			1																											
U. of Rochester	1		1																														
Vassar Coll.	1		1						1													2		1		1					6	4	1
North Carolina:																																	2
Duke U.	5	5	4																												2	4	3
N. C. State Coll.																																	
U. of N. C.	1	5	2																						1	3	2				3	8	1
North Dakota:																																	
N. D. Agr. Coll.			1																							1							1
Ohio:																																	
Case Sch. Appl. Sci.	2		2						1																						1		2
Kenyon Coll.																																	1
Oberlin Coll.			1		1	1															1					1					1		1
Ohio State U.	1	12	2		5	1													1			1	5	2	1	5	2	3	2	3	12	25	8
Ohio Wesleyan																											2						1
U. of Akron			1	1					1																	1							1
U. of Cincinnati	2	2	3																					1	1	1	3	1	2		5	5	2
U. of Dayton			1																														1
Western Reserve U.	6	3	1			1		1	1				1	2								3	10	1			2				6	1	1
Oklahoma:																																	
Okla. A. & M. Coll.	2		4																												2		
U. of Oklahoma	5	1	2																				1		1	1	1				5	2	1 2
Oregon:																																	
Ore. State Agr. Coll.	4	2	3	1		1							1												2		1				4		1
Pennsylvania:																																	
Bryn Mawr Coll.	1	1	1																														1
Bucknell U.																																	2
Carnegie Inst. Tech.	5	5	2								1	1																					
Dickinson Coll.			1																				1								4	1	1
Grove City Coll.			2																														
Haverford Coll.			3																														
Lafayette Coll.				2		1																	1										
Lehigh U.	3		4	1		1				1		1												2	1		1	2		4		1	2
Penn. State Coll.	2	8	4																			4	6	4	2		1		2	4	15	20	5
Swarthmore Coll.			1														1																6
U. of Penn.	1	3	7				2	3	1					2								3		1	4		4				9	3	3
U. of Pittsburgh	2	7	2														1	1						1		1	1	1	2	2	1	6	5
Rhode Island:																																	9
Brown U.		8	2																														
R. I. State Coll.	1		3				1						1							4	2			1	1		2				1	1	3
South Dakota:																																	
S. D. St. C. A. & M.	1																								1						1		
S. D. St. Sch. Mines																																	
U. of S. D.	2		1																												3		1
Tennessee:																																	
Geo. Peabody Coll.	1																																
U. of Tenn.	5		2																												8		2
Vanderbilt U.	2	1	1			1																				1	1	1	1	1	1	3	2
Texas:																																	
A. & M. Coll.	1																								1								
Baylor U.	1																								1								
Rice Inst.	1	1	1	3	1	1																	1								1		
U. of Texas	1	9	2																												3		1
Utah:																									1						10	18	3
U. State Agr. Coll.																																	
U. of Utah	3		2																			1			3		2	6		4			
Vermont:																																	
Middlebury Coll.			1																														
U. of Vermont	2		3																												3		1
Virginia:																																	
U. of Va.	1	13	5					1																	1	1	2				5	9	9
Va. Poly. Inst.			1	1		1																					1		1		3		1
Wash. & Lee U.																						1		1							2		2
Washington:																																	
State Coll. Wash.	1	1	2	1		1							3	1		1		1	1	1	1			1				1		1	1		1
U. of Wash.	1	7	2		1								1										1	2	7	3	2				8	8	2
West Virginia:																																	
W. Va. U.				1	1	1										1	1														1	2	3
Wisconsin:																																	
Inst. Paper Chem.			1	2	2	4																					2				3		3
Lawrence Coll.						1																											1
Marquette Med. Sch.																											2						
U. of Wis.	5	11	8		14	4		3	2								1			3	1	1	4	2	4	2	1				7	25	10
Wyoming:																																	
U. of Wyo.																1	1																1
TOTALS	171	331	283	31	65	54	12	14	17	3	27	20	14	23	9	5	4	9	11	39	28	71	79	73	75	75	92	43	26	38	374	570	334

Physiological M	Physiological D	Physiological F	Pharmacological M	Pharmacological D	Pharmacological F	Pharmaceutical M	Pharmaceutical D	Pharmaceutical F	Sanitary M	Sanitary D	Sanitary F	Nutrition M	Nutrition D	Nutrition F	Foods M	Foods D	Foods F	Agricultural M	Agricultural D	Agricultural F	Industrial and Engineering M	Industrial and Engineering D	Industrial and Engineering F	Chemical Engineering M	Chemical Engineering D	Chemical Engineering F	TOTALS M	TOTALS D	TOTALS F	Universities by States
		1											1					1	1	2	1		1				11	14	12	*Nebraska:* U. of Neb.
1		1																									1		4	*Nevada:* U. of Nev.
		1																1		4							3		1	*New Hampshire:* Dartmouth Coll.
																											6		11	U. of N. H.
																								3		3	15	6	27	*New Jersey:* Princeton U.
																											8	8	3	Rutgers U.
													1			1				2									4	*New Mexico:* N. M. C. A. & M. A.
		2																											2	*New York:* Albany Med. Coll.
	3	9											4	8				1		1				13	42	8	13	122	76	Columbia U.
4	4	3																1			3	5	2				16	43	14	Cornell U.
3	4	6																						2	2	1	8	12	9	Fordham U.
																											2	2	1	N. Y. S. Coll. For.
				1						1											2		2				27	31	17	N. Y. U.
																						2	2		2	1	18	14	11	Poly. Inst. Brooklyn
1		2																						2	1	1	5	4	7	Rensselaer Poly.
		1																						4		2	16	11	9	Syracuse U.
2	9	24										4	2	3													15	16	30	Union Coll.
																											1		4	U. of Rochester; Vassar Coll.
	4	10											2					1		2							8	13	21	*North Carolina:* Duke U.
																		1												N. C. State Coll.
																					2	2	1	1		2	8	18	8	U. of N. C.
																							1						4	*North Dakota:* N. D. Agr. Coll.
																					3		2			2	6		9	*Ohio:* Case Sch. Appl. Sci.
2																													1	Kenyon Coll.
3	1	3		1	1								2	1	1	1	1	2		1	7	5	1	10	5	3	3	1	5	Oberlin Coll.
																											41	70	29	Ohio State U.
																					3								3	Ohio Wesleyan
																											4		4	U. of Akron
		1																			2		2	2		1	13	8	14	U. of Cincinnati
5	3	4																											3	U. of Dayton
																											21	20	11	Western Reserve U.
		2										1								2			2	2			8	1	13	*Oklahoma:* Okla. A. & M. Coll.
																											10	3	5	U. of Oklahoma
3	1	2		1			2											4		1			1			1	19	3	14	*Oregon:* Ore. State Agr. Coll.
																											1	1	2	*Pennsylvania:* Bryn Mawr Coll.
																													2	Bucknell U.
																						2					10	7	7	Carnegie Inst. Tech.
																													1	Dickinson Coll.
																													2	Grove City Coll.
																											1		3	Haverford Coll.
		1																									2		3	Lafayette Coll.
5	2	1										5	5	3			3	8	5	6	6		2	3		2	21		20	Lehigh U.
																					3	6	12	8	2	5	54	54	48	Penn. State Coll.
1	4	15																											5	Swarthmore Coll.
	1	4		3			1	1					4	3	1	1										1	20	13	36	U. of Penn.
																								6	2	2	11	26	29	U. of Pittsburgh
																		1	2	3							2	13	10	*Rhode Island:* Brown U.
																											4	2	6	R. I. State Coll.
1																											4			*South Dakota:* S. D. St. C. A. & M.
																		2		1							2		1	S. D. St. Sch. Mines
2		1																									7		3	U. of S. D.
															5			1									7			*Tennessee:* Geo. Peabody Coll.
	2	3																												
	1	4																						3		2	16	2	9	U. of Tenn.
																											4	7	10	Vanderbilt U.
1																								5			8			*Texas:* A. & M. Coll.
																											3			Baylor U.
		1																						1		1	8	2	6	Rice Inst.
1		3						1				2												13		1	28	27	10	U. of Texas
3		1										1		2	2		1	2		2							8		6	*Utah:* U. State Agr. Coll.
																											13		8	U. of Utah
																											3		2	*Vermont:* Middlebury Coll.
3		2																									5		5	U. of Vermont
		2																		3	1		1	4		1	7	24	19	*Virginia:* U. of Va.
																										2	10		11	Va. Poly. Inst.
																											3		3	Wash. & Lee U.
3		3						3				3	1	7			4	3	4	10							18	8	35	*Washington:* State Coll. Wash.
	4	1																				1		5	2	3	22	27	12	U. of Wash.
				2															2	1	4		1				7	5	9	*West Virginia:* W. Va. U.
																					4	1	4		2		9	5	14	*Wisconsin:* Inst. Paper Chem.
																													2	Lawrence Coll.
		3																											5	Marquette Med. Sch.
5	4	6	2	4	3	4	4	4	4		1				4	1	1				2	1	5		5	4	38	82	52	U. of Wis.
1		1																									2		3	*Wyoming:* U. of Wyo.
108	177	251	4	10	32	12	14	25	15	4	8	55	50	72	33	15	24	72	67	86	74	28	52	228	130	100	1411	1748	1607	*TOTALS*

THE NEW CHEMISTRY BUILDING AT THE UNIVERSITY OF ARKANSAS

THIS new building on the campus at Fayetteville was occupied in the fall of 1935, at the same time that the new University Library was opened. Both buildings were planned in 1931, and have now been financed by the PWA. The cost of the Chemistry Building is a little more than a half-million dollars. It was dedicated on June 10, 1935, during the Commencement Week. The principal speaker was Dr. Edward Bartow, then president-elect of the American Chemical Society, whose subject was the "House of Chemistry."

The building is E-shaped, 257 feet in its longest dimension. The longest wing is 105 feet in length. The four floors, including the basement, contain more than 60,000 square feet, divided into somewhat more than one hundred rooms. The framework is of concrete, and the exterior includes Carthage and Indiana limestone. The laboratories have white brick walls.

While eventually the entire building will be used for chemistry and chemical engineering, it will house temporarily the departments of geology, zoölogy, and philosophy and psychology, which will occupy parts of each floor, into which chemistry will later expand. Rooms for chemical and apparatus storage are provided in the basement. A special room or cave for inflammable organic chemicals occupies one corner, and there are special rooms for the supply of direct current and of hydrogen sulfide, which will be carried to various parts of the building. The south half of the basement has daylight, and includes a lecture-demonstration room and a laboratory for water analysis and space for chemical engineering. The main auditorium is located in the middle wing of the first floor. It has a sloping floor and a seating capacity of 277. The lecture table is partly permanent and partly movable on wheels. It is lighted with floodlights from the ceiling, which are completely concealed from the view of the audience. In addition to the two lecture rooms there are five recitation rooms throughout the building. The first floor contains also the main offices and the laboratories for general chemistry, physical chemistry, and inorganic preparations. Laboratories for qualitative analysis and quantitative analysis occupy the east half of the second floor. The departmental library and reading room are in the middle wing over the auditorium. Organic chemistry occupies the east half of the third floor.

The two lecture rooms are provided with storage space for chemicals and for lecture and display materials. Adjacent to each of the larger laboratories is a preparation room equipped for the storage of necessary chemicals and for the making up of solutions. There is a dispensing room on each floor for the handling of apparatus. These are directly over each other and are connected with a freight elevator with a door into the dispensing room and also into the corridor. In each of these rooms there are two service windows, one into the largest laboratory on that floor and the other into an alcove off the corridor. The hoods in the laboratories are operated by fans with remote control. There is additional provision for the frequent changing of the air and for warming the incoming air in cold weather. While the best interests of the undergraduate have been kept to the fore, the advanced student has not been neglected. Each instructor's office is adjacent to a private research laboratory, and there are several other research laboratories, each of which will accommodate one or two students.

A. T. Burtsell
F. B. Dains
Tenney L. Davis
Spurgeon Gage
J. Howard Graham
B. Clifford Hendricks

ABSTRACTS

R. A. Baker, *Abstract Editor*

J. W. Howard
D. C. Lichtenwalner

Greta Oppe
C. M. Pruitt
Leopold Scheflan
E. D. Walter
Sidney Weinhouse
G. H. Woollett

KEEPING UP WITH CHEMISTRY

How soy beans help build Fords. R. L. Taylor. *Chem. & Met. Eng.*, **43,** 172–6 (Apr., 1936).—Mr. Ford became interested in soy beans as a result of his search for some product of the soil which could be used in the manufacture of automobiles. The process developed is one of cold extraction at atmospheric pressure involving a continuous unit with a capacity of 500 lb. of beans per hour and capable of operation by one man. The entire unit consists of a flaker, continuous extractor, filter, and solvent-recovery system. At the present time the solvent used is hexane, with a loss of about 1 lb. per 100 lb. of beans. The cost of the entire unit is well within the reach of rural coöperatives. The oil removed by the solvent is used as an enamel vehicle and in the manufacture of glyptal resin which serves as the base of body enamel. Some is used in the foundry as a sand-core binder.

The extraction process leaves a meal containing 48% protein, the major portion of which is casein, 38% carbohydrates, 7% cellulose, and 7% ash. The casein is used to make a phenol-casein-formaldehyde plastic. The entire meal is used for this as the other substances present make a good filler. Wood flour is used as an additional filler. This plastic is used to make distributor parts, gear shift lever knobs, light switches, horn buttons, coil parts, and window frames.

For the production of one million automobiles the company will require 450,000 bushels of soy beans—the product of 28,000 acres. J. W. H.

A new safety glass. J. H. Sherts and E. L. Fix. *Chem. & Met. Eng.*, **43,** 177–9 (Apr., 1936).—A new type of safety glass has been developed by the joint work of the Duplate Company and the Carbide and Chemicals Corp.

In the older types of safety glass cellulose nitrate is used as the interlayer. This developed a brown discoloration after a year or two of service due to the actinic rays of the sun. This has been overcome in part by substituting cellulose acetate, or by using a special filtering glass which has a higher iron content than ordinary glass. The addition of iron also imparts a cast to the glass which reduces road and general reflection glare. But even these glasses had certain drawbacks.

In the latest safety glass a new resin called "Vinylite X" and a plasticizer are used. The two ingredients are mixed and converted into sheets approximately 0.025 inch thick. These sheets are placed between clean plates of glass and subjected to heat and pressure. This product shows no discoloration after 1000 hours' exposure to the Uviarc test. It will not decompose in 320 hours at 260°F.—hence glazed automobiles can be passed through enamel-baking ovens without damaging the new safety glass. J. W. H.

Magnesium compounds from ocean water. H. H. Chesny. *Ind. Eng. Chem.*, **28,** 383–90 (Apr., 1936).—Three years ago commercial recovery of Br was begun in the Atlantic Ocean; here we have a description of a plant on the Pacific to recover Mg from sea water containing about 0.1% Mg as compared to 12% in dolomite and 28% in magnesite, and brines of high Mg content. This can be done since there are no drilling and deep well maintenance costs, and since the removal of concentrated impurities is costly.

Theoretically, the production of magnesium compounds from sea water is made possible by the fact that magnesium hydroxide is practically insoluble in water (0.34 pound per 1000 gallons at 60°F. for the *alpha* and 0.078 for the *beta* modification). Consequently, the addition of an alkali to a solution of a magnesium salt, no matter how dilute, will permit a nearly theoretical yield of magnesium hydroxide. From a practical point of view, the successful production of magnesia from sea water depends upon:

(1) the means to soften the sea water cheaply;
(2) the preparation of a purified lime slurry of proper reactivity and ability to maintain the chemical and physical characteristics of the slurry constant at all times;
(3) the economical removal of the precipitated hydroxide from the large volume of water;
(4) the inexpensive purification of hydrous precipitates;
(5) the development of means to filter the viscous slimes.

The recovery of Mg salts is based on the precipitation of $Mg(OH)_2$ from $MgCl_2$ and $MgSO_4$. Fifty-five gallons of sea water is required to produce 1 pound of MgO on the basis of 100% yield. Purification and plant operation are discussed. Suggested uses are replacement of NaOH in many operations, oil purification, and necessity of using Mg in fertilizers. D. C. L.

Economics of synthetic rubber. E. R. Bridgwater. *Ind. Eng. Chem.*, **28,** 394–8 (Apr., 1936).—Within the past five years a synthetic rubber industry has arisen in Soviet Russia and in the United States. It is also reported that synthetic rubber is being produced on a small scale in Germany. Both the Soviet butadiene rubber and the American chloroprene rubber are discussed, because the synthetic rubber industry is being developed in Russia and in America under economic conditions that are diametrically opposite to each other.

Average cost of production of natural rubber is probably about 5 cents per pound. The latex has a variable composition depending on the soil, age of trees, season of the year, and other factors. Rubber made in Russia from butadiene, produced by high-temperature cracking of ethyl alcohol, seems to be inferior to natural rubber. Twenty thousand tons was produced in 1935. Costs are not available. Yield has been increased from 14.4% to 23%.

DuPrene is made by the polymerization of chloroprene, 2-chloro-1,3-butadiene (2), which is made by the addition of HCl to monovinylacetylene (5). The latter compound is made by the polymerization of C_2H_2 in the presence of a catalyst consisting essentially of a saturated aqueous CuCl and NH_4Cl. It might appear that DuPrene is potentially capable of being produced as cheaply as natural rubber, but such is not the case. If the conversions of C_2H_2 to monovinylacetylene, to chloroprene, and chloroprene to its plastic polymer, DuPrene, could all be carried to completion without the formation of any by-product, we would obtain 1.7 pounds of DuPrene from a pound of C_2H_2 and 0.7 pound HCl. The process is interrupted before complete conversion to avoid the formation of a tough product.

DuPrene, compounded and vulcanized, is more resistant to abrasion, more resistant to oils, oxidation, high temperature, and diffusion of gases than products made from natural rubber. D. C. L.

Latest transparent wrap. Anon. *Ind. Bull. Arthur D. Little, Inc.*, **111,** 4 (Apr., 1936).—The latest transparent wrap is a new protective coating for underground pipe. The pipe is first coated with asphalt, then two separate layers of Kodapak (Eastman's cellulose acetate transparent film), followed by more asphalt and, finally, paper. When the paper or wrapping is squeezed or rubbed by the surrounding soil, the two layers of Kodapak slide on each other and the two underlying protective coats of asphalt remain intact. The purpose of this novel coating is protection against soil stresses that formerly cracked the protective layer and permitted corrosion. G. O.

Oiticica oil. Anon. *Ind. Bull. Arthur D. Little, Inc.*, **111,** 3–4 (Apr., 1936).—Because Chinawood oil, or "tung" oil, as it is frequently called, is not produced in sufficient quantity to furnish a dependable day-by-day supply of this type of oil, an oil of Brazil, called oiticica, offers a useful solution to the problem of maintaining a sufficient supply of low-priced oil for our varnish industry. Oiticica oil is obtained from a nut of a tree related to the tung-oil tree. Chemically, it is also similar. The oil is thickish, almost buttery, but may be made fluid by being subjected to heat treatment. Like tung oil, it absorbs oxygen vigor-

ously. Up to the present, it has not been found possible to produce the highest grade of varnishes and enamels from oiticica oil alone, but as much as three-fourths may be used with one-fourth Chinawood oil. It is rated somewhat below tung oil in quality and therefore sells at a somewhat lower price than tung oil. These trees, too, must be of considerable age before they bear fruit. Those being harvested now in Brazil are upwards of one hundred years of age, and may yield from one to nearly two tons of oil, per tree, in good years. For the present, the oil comes into the U. S. tax-free. G. O.

APPARATUS, DEMONSTRATIONS, AND LABORATORY PRACTICE

Yellow phosphorus from bones. G. H. LOCKET. *Sch. Sci. Rev.*, **17**, 296 (Dec., 1935).—Student laboratory preparation. The bones are calcined in a muffle or central heating furnace. About 300 g. of the ash, finely powdered, is added, small quantities at a time, to 320 g. (175 cc.) of sulfuric acid diluted with its own volume of water. The mixture is heated, with occasional stirring, on the water bath for an hour or two, water being added if necessary. After cooling, it is filtered at the pump, and the solid washed with 1.5 liters of water. The filtrate is then evaporated, and when it is of a sirupy consistency, powdered charcoal is added and the mixture worked up with a rod into balls, which harden on cooling, and constitute the charge for the retort. The retort is made from standard gas tubing 2 inches in diameter and 5 inches long, with threads on each end onto which screw two caps. One of these carries a reducing socket with a piece of $^5/_8$-inch tubing bent at right angles. The retort is loosely packed, the threads are covered with a paste of litharge and lead carbonate mixed with linseed oil, and the ends are screwed on. The retort should be left to stand a day, then placed in a muffle, the delivery tube passing into a pyrex distilling flask through a plug made of asbestos soaked in phosphoric acid and covered with zinc oxide. A rubber tube attached to the side tube leads under water to form a seal.

During distillation the receiver is immersed in cold water, which is allowed to get hot and is not changed. Reducing gases and steam soon pass over and the temperature is slowly raised as high as possible, the distillation taking 2.5–3 hours. The end of the retort should be removed as soon as possible after use. If it is warmed on a gas-ring, it can be shifted quite easily with a spanner and a wooden mallet.

The yellow phosphorus is left with dilute chromic acid for a day and after washing and melting, is drawn through a warm tube, fitted with a glass-wool filter, into a test-tube with water. Usually a perfectly white product is obtained. Yields about 15–20% of theory. S. W.

Phosphates. A. W. WELLINGS. *Sch. Sci. Rev.*, **17**, 460 (Mar., 1936).—Soluble orthophosphates can be titrated in neutral or weakly acidic solution with standard lead acetate in the presence of dibromofluorescein as an adsorption indicator. Alkaline phosphates are first neutralized with nitric acid, using phenolphthalein as the indicator; 2 or 3 drops of a 1% solution of dibromofluorescein are then added, and the titration with lead acetate carried out until a permanent pink coloration is obtained on the precipitate of lead orthophosphate. The best concentrations of phosphate and lead acetate lie between 0.1 and 0.05 molar. S. W.

The two-component system *p*-toluidine-α-naphthol. F. BRIERS. *Sch. Sci. Rev.*, **17**, 461 (Mar., 1936).—This system is ideally suited to illustrate the occurrence of eutectics and compounds in systems of two components. Mixtures of varying composition are melted, allowed to cool with efficient stirring, and the initial temperature of solidification noted. The plot of these temperatures against the composition gives the following fixed melting points: *p*-toluidine, 43°C.; α-naphthol, 94°; compound *p*-toluidine-α-naphthol, 50°; eutectic No. 1, 26°; eutectic No. 2, 47°. The percentages of *p*-toluidine in 3, 4, and 5 are approximately 42.6, 75.5, and 33. S. W.

ADMINISTRATIVE PROBLEMS AND DEVICES; CURRICULA

Honors seminar at Louisville. E. C. HASSOLD. *J. Higher Educ.*, **7**, 137–40 (Mar., 1936).—One of the striking recent developments in American higher education is the opportunity for superior students to do honors work or independent study. This honors work runs in the main to two types. In the one, the student is given leisure and guidance to cover the established departmental pensum or that pensum plus, in his own way and at his own pace. The ideal goal of this type of honors work is the performance either of the same work in less time or of additional work in the same time as is usually required for a bachelor's degree. In the other type, this speeding up process is accompanied by some sort of integration of study in related fields. The ideal goal of this type, in which Swarthmore and Harvard are leading the way, is intellectual maturity together with proficiency in the field of concentration.

The College of Liberal Arts of the University of Louisville, in addition to providing for honors work in both these types, has for the past two years been experimenting with a third type of honors work. It is the purpose of this article to describe the honors seminar at Louisville and its aim.

A small number of the best students was to meet with from two to six faculty members once a week to discuss for two hours or more some subject of broad common interest. The selection of the students was to be based on high marks, excellent performance in national tests, and recommendations for intellectual ability by instructors. The seminar was conceived of primarily as an intellectual mixer.

The subject matter chosen was in keeping with Lincoln Steffens' point of view: frontiers of knowledge. The method used was twofold: there were discussions led by faculty members, and book reviews, chiefly by students, of books projecting lines into the future. Those read in one seminar were Bertrand Russell, "The Scientific Outlook"; Kilpatrick and Others, "Frontiers in Education"; Saylor, "Revolt in the Arts"; and Spengler, "The Hour of Decision." After a preliminary investigation of pertinent bibliography, each reviewer chose his own book. The rest read as many of the books reviewed as they could or cared to. Credit from one to three hours was given, according to the number and variety of books on which the student took an examination; the rest of the examination consisted of an essay on the student's view of the future.

The honors seminar brought out that even under our divisional organization our best students tend to confine their interests to their major. A. T. B.

SCIENTIFIC REVIEWS AND BIBLIOGRAPHIES; TABULATIONS OF SCIENTIFIC DATA

The theory and practice of adsorption indicators. A. W. WELLINGS. *Sch. Sci. Rev.*, **17**, 181–90 (Dec., 1935).—The introduction of adsorption indicators has marked a decided advance in the technic of precipitation methods in volumetric analysis. The task of placing this new method of analysis on a theoretical basis was accomplished by Fajans as the result of a detailed examination of the phenomena occurring in the adsorption of dyestuffs. Lottermoser, in 1905, showed that when KCl is precipitated with $AgNO_3$ the precipitate of AgCl exhibited a negative charge with respect to the solution if KCl were present in excess, and a positive charge if $AgNO_3$ were in excess. It was therefore reasonable to assume that the original charge on the precipitate is due to the adsorption of Cl or Ag ions, respectively, from the solution on the ion-lattice of the precipitate. In the titration of Cl with Ag in the presence of fluorescein, the solution retains the greenish yellow color of the dye and the precipitate of AgCl remains white until the equivalent amount of Ag is added. On the addition of one more drop the excess Ag ions are adsorbed, forming the complex, (AgCl)Ag, which then adsorbs the negative fluorescein ion. The fluorescein anion, when in the adsorbed condition, exhibits a different (pink) color, and thus the adsorption of the indicator is made visible. This process is typical of most adsorption indicators.

In order to obtain an effective color change, most of the dye ions must be adsorbed at the equivalent point. In general, 10^{-3} moles of dyestuff per mole of silver halide precipitated is a practical value. A very common error is to take too high a concentration of indicator solution. The lower the concentration of indicator used, the more exact will be the color change. With a basic indicator the same principles are found to apply, though in this case the effective ion is the dye cation. A summary of the chief titration methods in common use is given in the following table. The particular conditions applying to each determination are given briefly.

Titration of	With	Indicator	Color change	Particular Conditions	Authority
Cl^-	Ag^+	Fluorescein	Yellow-green ⟶ pink	Soln. neutral or slightly alkaline. Not possible below 0.005 *N*.	Fajans and Wolff Kolthoff and v. Berk
		Dichlorofluorescein	Yellow-green ⟶ orange-red	In 0.025 *N* Cl^- in acid soln. up to pH ~4, and in the presence of heavy metals. In neutral soln. down to 0.0005 *N* to 1–2 per cent.	Kolthoff, Lauer, and Sunde
		Brillant-Orseille C	Red ⟶ blue-green	Down to 0.005 *N* Cl^- in the presence of acetic acid, and also in the presence of 0.5 g. of $MgSO_4$. In 0.01 *N* HNO_3 to the same degree of accuracy.	Belladen and Piazza
		Phenosafranine	Red (ppt.) ⟶ blue (ppt.)	See Br^-; less sharp endpoint.	Berry and Durrant Fajans and Weir
		Diphenylamine-blue	Green (ppt.) ⟶ violet (soln.)	In concentrations 0.01 *N* Cl^- in the presence of 5 *N* H_2SO_4.	Lang and Messinger
		Bromophenol-blue	Yellow-green ⟶ green-blue	In acetic acid soln., green endpoint not sharp.	Kolthoff
Br^-	Ag^+	Fluorescein	Yellow-green ⟶ pink	As with Cl^-, but not so good as eosin.	Fajans and Wolff
		Eosin	Yellow-red ⟶ red-violet (depending on concs.)	Down to 0.0005 *N* Br^- in acid soln., pH > 1. Best in acetic acid soln.	Fajans and Wolff Kolthoff
		Chromotrope F_4B	Red ⟶ grey (red reflex)	Down to 0.01 *N* in acetic acid soln. Not in the presence of other cations.	Belladen and Piazza
		Brillant-Orseille C	Red ⟶ grey-green	As with Cl^-, but also in the presence of 0.02 *N* HNO_3 accurately.	Belladen and Piazza
		Phenosafranine	Red (ppt.) ⟶ blue (ppt.)	Only in the presence of NO_3^-, or CO_3^{--}; also in mixtures containing Zn^{++}, Pb^{++}, Cd^{++}, or HNO_2.	Berry and Durrant Fajans and Weir
		Diphenylamine-blue	As with Cl^-		Lang and Messinger
	Hg^+	Bromophenol-blue	Yellow (ppt.) ⟶ lilac (ppt.)	0.1 *N* Br^- solns. can be titrated with 0.1 *N* $HgNO_3$ in dil. HNO_3. Endpoint quite sharp.	Burstein
I^-	Ag^+	Fluorescein and derivatives tabulated separately			
I^-	Ag^+	Erythrosin	Red ⟶ red-violet	Only accurate in the presence of other salts of higher valency; *e. g.*, a twenty-fold excess of $MnSO_4$.	Rudenko
		Chromotrope F_4B	Pink ⟶ green	Down to 0.01 *N* in the presence of 0.01 *N* HNO_3.	Belladen and Piazza
		Brillant-Orseille C	Pink-violet ⟶ grey-green	As with Br^-.	Belladen and Piazza
I^- in presence of Cl^-	Ag^+	Eosin	Yellow-red ⟶ red-violet	In the presence of ammonium carbonate (which dissolves AgCl), I^- is determined exactly in the presence of Cl^- with all four indicators.	Kolthoff Fajans, Hassel, and Wolff
		Di-iodofluorescein	Orange ⟶ red		
		Dimethyl-diiodofluor	Orange-red ⟶ carmine		
		Rose Bengale	Carmine ⟶ blue-violet		
		Chromotrope F_4B Brillant-Orseille C	Red ⟶ grey-green	Endpoint in colloidal soln. corresponds nearly to that of I^- alone; best in presence of ammonium carbonate.	Belladen and Piazza
$I^- + Cl^-$	Ag^+	Fluorescein	Yellow-green ⟶ red-green ⟶ red	Endpoint not sharp; obtained best in admixture with excess Ag^+ and back-titration with Cl^-. Error ± 1 per cent.	Fajans and Wolff
		Dichlorofluorescein	Yellow-green ⟶ yellow-brown ⟶ orange-brown	Not sharp; accurate to 0.5 per cent. in 0.1 *N* halide soln.	Kolthoff, Lauer, and Sunde
		Bromophenol-blue	Yellow ⟶ green	Down to 0.01 *N* in acetic soln. in the presence of dextrin. Correct to 0.5 per cent.	Kolthoff
		Tartrazine	Colorless (soln.) ⟶ green (soln.)	Precipitation with small excess Ag^+ and back-titration with I^-. Very sharp.	Berry and Durrant
CN^-	Ag^+	Diphenyl-carbazide	Pink ⟶ violet	Very sharp; very exact down to 0.00001 *N* CN^- with 0.005 *N* $AgNO_3$.	Wellings
		Fluorescein	Yellow-green ⟶ red	Only in the presence of excess $NaHCO_3$; not very sharp.	Kolthoff
CNS^-	Ag^+	Fluorescein	As with Cl^-		Fajans and Wolff
		Eosin	As with Br^-		Kolthoff and v. Berk Kolthoff
$CNSe^-$	Ag^+	Fluorescein	Yellow-green ⟶ red	Down to 0.005 *N*.	Ripan
$Fe(CN)_6^{++}$	Ag^+	Fluorescein	Yellow-green ⟶ red	Only in the presence of excess $NaHCO_3$; not very sharp.	Berry and Durrant
	Pb^{++}	Alizarin S	Yellow ⟶ red	Best in *N*/30 or *N*/60 solns. of ferrocyanide.	Burstein
OH^-	Pb^{++}	Fluorescein	Yellow-green ⟶ pink	Quite sharp in 0.01 *N* and 0.1 *N* solns.	Wellings
$C_2O_4^{--}$	Pb^{++}	Fluorescein	Yellow-green ⟶ pink	In neutral soln. down to 0.01 *N*	Wellings
BO_2^- and $B_4O_7^{--}$	Pb^{++}	Dichlorofluorescein	Yellow-green ⟶ red	Meta-borates, ortho-borates, and "perborates," can be titrated down to 0.01 *N*. Very accurate in neutral soln.	Wellings
SO_4^{--}	$Ba(OH)_2$	Fluorescein	Yellow-green ⟶ pink ⟶ orange	$MgSO_4$ and $MnSO_4$ can be titrated directly in 0.1 *N* soln. Change occurs on ppt. of $Mg(OH)_2$ or $Mn(OH)_2$. Other sulfates indirectly in the presence of magnesium or manganous acetate. Neutral solns.	Wellings
NO_3^-	Ti^{+++}	Alizarin	Pink ⟶ grey-green	0.1 *N* solns. of nitrates are titrated with $TiCl_3$ (in HCl) in an atmosphere of hydrogen (as in ordinary ferric iron titration). The color change occurs on a ppt. of $Ti(OH)_4$ formed by hydrolysis; the soln. must be boiled after each addition of $TiCl_3$. 3 atoms of Ti are equivalent to one molecule of HNO_3.	Wellings
Ag^+	Br^-	Rhodamine 6 G	Yellow-red ⟶ red-violet	Down to 0.1 *N* Ag^+ in the presence of 0.5 *N* HNO_3. Quite sharp.	Fajans and Wolff Kolthoff
		Brillant-Orseille C	Green ⟶ pink	Down to 0.005 *N* Ag^+ in the presence of *N*/3 HNO_3.	Belladen and Piazza
		Phenosafranine	Blue (ppt.) ⟶ red (ppt.)	See Br^-.	
		Tartrazine	Yellow ppt. (or colorless soln.) ⟶ green soln.	In 0.1 *N* soln., also in the presence of 0.5 *N* HNO_3, and Pb^{++}, Cd^{++}, or Zn^{++}.	Berry and Durrant
	Cl^-	"			
	CNS^-	"	Colorless (soln.) ⟶ green (soln.)	0.1 *N* solns.	Kolthoff
	I^-	"			
Pb^{++}	CrO_4^{--}	Orthochrome T	Green (soln.) ⟶ wine-red (soln.)	In neutral 0.02 *N* soln.	Fajans and Weir
PO_4^{---}	Pb^{++}	Dibromofluorescein	Orange ⟶ pink	Orthophosphates may be titrated with lead acetate in slightly acid solution, down to 0.005 *N*.	Wellings

Notes on Table—The dyestuff Brilliant-Orseille C used by Belladen and Piazza is identical with Brilliant Archil C (Brilliant Wool Scarlet). Where Pb^{++} is given as the precipitating ion it is best to use lead acetate. The titration of SO_4^{--} with $Ba(OH)_2$ must not be performed in yellow artificial light.

S. W.

RECENT BOOKS

ANTOINE LAVOISIER, THE FATHER OF MODERN CHEMISTRY. *Douglas McKie*, Ph.D., B.Sc., A.I.C., Lecturer in the Department of History and Methods of Science, University College, London; with an introduction by *F. G. Donnan*, C.B.E., LL.D., D.Sc., F.R.S., Professor of Chemistry in the University of London. J. B. Lippincott Company, Philadelphia, 1936. 303 pp. 7 illustrations. 12.8 × 20.9 cm. $2.50.

This book fills a need that has long existed by supplying in the English language an excellent account of the life of Lavoisier and of his chemical ideas and investigations. It is thoroughly up to date, and contains an adequate treatment of the recent researches of Professor Andrew N. Meldrum on Lavoisier's early work. It mentions a number of things which have not yet found their way into the histories of chemistry, and perhaps for the first time sets the various researches of Lavoisier in their proper chronological sequence. Sources are everywhere clearly indicated.

The first chapter, I. Biographical, and the last, IX. Last Years, 1789–94, treat largely of the personal history of Lavoisier, but his public and scientific activities made up so great a part of his later life that the last chapter seems rather to deal with them. It somehow brings home in a new way the dismay of the French Revolution, the utter impotence of the integrity of Lavoisier, its irrelevance to the troubled times. The first chapter tells of his family background, of his young manhood and studies in geology and mineralogy, of his election to the Academy, of his preparation for that body of many reports on scientific subjects truly too numerous to mention, of his entrance into the *Ferme*, of his marriage at the age of twenty-eight to a bride of fourteen years, and of his work on saltpeter and gunpowder, which was not without some relation to his tragic end.

The second chapter, II. Lavoisier's Chemical Heritage, describes briefly the state of chemical science before his time, Boyle, phlogiston, and Black. The others describe Lavoisier's work, but they also tell of his contacts with men of science and with the social and political forces among which he was living, and give a very good idea of his times. They are headed as follows—III. Early Researches: The Nature of Water, Its Alleged Conversion into Earth, the Combustion of the Diamond; IV. Combustion and Calcination: the *Opuscules Physiques et Chimiques;* V. Priestley's Isolation and Recognition of Oxygen; VI. Lavoisier's Memoirs, 1774–5, and their Revision: The New Theory, 1777–8; VII. Development of the New Theory, 1778–86; and VIII. The *Nomenclature Chimique* (1787) and the *Traité Élémentaire de Chimie* (1789). The book is sound and scholarly and is written in a pleasant narrative style. It ought to appeal to young students and old, and to any who are interested in history. It can be read with pleasure by high-school students and with profit by those who have graduated from college.

The author is one of the three Editors of the *Annals of Science*, a new quarterly review of the history of science since the Renaissance, the first number of which appeared on January 15, 1936.

TENNEY L. DAVIS

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

DIE QUANTITATIVE ORGANISCHE MIKROANALYSE. *Fritz Pregl;* revised and rewritten by *Hubert Roth.* Fourth edition. Julius Springer, Berlin W 9, 1936. xiii + 328 pp. 16 × 24 cm. RM 24; bound, RM 26.

The fourth edition of *Quantitative Organic Microanalysis* has been published by Dr. Hubert Roth, a colleague of the late Dr. Fritz Pregl. With the exception of numerous quotations from the third edition, the book has been entirely rewritten by Dr. Roth. Many new procedures have been added and each method is given under the name of its author in order to distinguish it from Professor Pregl's own work. The notes on the purification of small amounts of materials have been omitted and the account of the historical development is much shorter. In general, the organization of the book is better, as related material has been assembled and appears in separate sections under appropriate titles.

The methods of determination given in the third edition have been carefully studied by Dr. Roth, and many valuable suggestions are given. The sources of error in the determination of carbon and hydrogen by the micro-combustion method are listed and new methods for the purification of reagents and improvements in general procedure are included. The following determinations are discussed in much more detailed form than in the third edition: micro-Kjeldahl volumetric determination of nitrogen, determination of methyl- and ethylimino-groups, Rast's method of molecular-weight determination by melting-point lowering, and Fischer's method of determination of rotatory power.

The following methods of determination appear for the first time in the fourth edition:

1. The alkalimetric determination of chlorine and bromine.
2. The titration of iodine as iodate.
3. The volumetric determination of sulfur in presence of nitrogen and halogen.
4. Simultaneous determination of halogen and sulfur.
5. Volumetric determination of phosphorus.
6. The determination of barium and phosphorus, as well as nitrogen and mercury, with one weighing.
7. The direct equivalent-weight determination.
8. The determination of active hydrogen.
9. The micro-Van Slyke method of determination.
10. The titration of amino acids.
11. The volumetric determination of alkoxyl-alkylimino and sulfur-methyl groups.
12. A simplified determination of acetyl-(benzoyl-) group.
13. The determination of isopropylidene group.
14. The determination of C-methyl groups.
15. The catalytic micro-hydrogenation.
16. The photoelectric measurement of absorption spectrum.
17. The micro-molecular refraction.
18. The molecular weight determination by isothermal distillation.
19. The melting point lowering under the microscope.
20. The boiling-point determination with small amount of substance.

ADELINE BLOODGOOD

THE UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

SOLUTIONS OF ELECTROLYTES. *Louis P. Hammett*, Ph.D., Professor of Chemistry in Columbia University. Second edition. McGraw-Hill Book Company, Inc., New York and London, 1936. ix + 238 pp. 11 figs. 13.5 × 20.5 cm. $2.25.

This book "is an attempt to make the fullest use of qualitative analysis as a means of teaching chemistry." By this is meant, of course, the chemistry of conducting solutions. It is a very able and attractive presentation of the theory of analytical chemistry. Dr. Hammett has a pleasing style that makes the subject logical and easily grasped.

The book is divided into two main parts, "Principles" and "Experiments." The latter "are intended to illustrate by sound examples of experimental method the principles discussed in the first part rather than to teach a definite scheme of analysis."

Part I begins with the fundamental laws and concepts upon which the practice of analysis is based. It also discusses the modern theory of acids and bases. But the idea is not dropped here. It is used in a simple, logical manner throughout the book. This constitutes an outstanding difference between Dr. Hammett's and other comparable texts. The remaining chapters deal, in excellent style, with the solubility-product principle, weak electrolytes (including chemical equilibrium), the ioniza-

tion of water (comprising also acidity, basicity, and hydrolysis), complex compounds, oxidation-reduction compounds, and oxidation potentials. In the latter chapter the use of the ambiguous term "molar potential" is regrettable. It may be justified in cases where the activity concept cannot well be taken up, but the term standard potential, with its precision and universality of meaning, is much to be preferred. Every chapter is followed by numerous questions and exercises and suggestions for supplementary reading.

Part II starts with a chapter of good advice. The sections on "The Estimation of Quantity" and "On Efficiency in the Laboratory" are worthy of particular mention. It is followed by the detailed course of instruction with many questions on the experiments. "The Method of Analysis" (scheme) comes next and is followed by an abundance of notes. A few additional methods conclude this section.

Appendix A details a great number of very good illustrative lecture experiments. Appendix B gives a suggested schedule of laboratory work, a list of reagents (with amounts per student) required, suggestions on suitable unknowns, and the student apparatus kit. The book also contains seven tables of useful data and a periodic table. Format, etc., meets the usual McGraw-Hill standard of excellence.

Every teacher of qualitative analysis will do well to consider this outstanding text for his course.

MALCOLM M. HARING

UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND

THE CHEMISTRY OF NATURAL PRODUCTS RELATED TO PHENANTHRENE. *L. F. Fieser*, Associate Professor of Chemistry, Harvard University. A. C. S. Monograph, No. 70. Reinhold Publishing Corporation, New York City, 1936. x + 358 pp. 341 figs. 15 × 23 cm. $6.50.

This monograph is fully justified by the vast amount of chemical research that has been conducted during recent years in different laboratories throughout the world on the chemistry of various physiologically active principles which are of great biological importance and which contain the same ring structure. This field of research has brought forward results which are of great interest to all engaged in scientific research. The purpose of the book is to furnish a comprehensive review of the latest achievements in the field of sterol chemistry. The author, who has been active in this field, has accomplished his task with a good measure of success. There can be no doubt about the thoroughness with which he has compiled the great number of references which bear on this subject.

In describing chemical investigations and in pointing out chemical relationships the author easily holds the reader's interest with a wealth of intriguing factual material. The descriptions of different physiologically active principles which belong to the group of sterols make up the major portion of the book. This section is preceded by three chapters in which the author gives an outline of the various methods that have been employed in the preparation of the phenanthrene ring structure and related hydrocarbons. In these chapters the author also discusses the chemistry of various natural products like the morphine alkaloids, the resin acids, and certain hydrocarbons which are characterized by their ability to produce cancerous growth. The next chapter gives a thorough description of the chemical work which finally culminated in the establishment of the structural formulas of the bile acids and the sterols like cholesterol and ergosterol. Chapter 5 contains a review on the chemical investigation of the various sex hormones; the chemical constitution of most of these has been definitely established. Chapter 6 deals with the chemistry of the heart poisons of either plant or animal origin. While the chemical structure of the plant cardiac glucosides has been fairly well established the exact chemical structures of the principles from toad poisons are still under investigation at present. The final chapter describes the saponins of the digitalis group. Recent chemical investigation has shown that they also are closely related to the sterols.

Throughout the book the author has not failed to point out the chemical interrelationships between these different groups of substances. The descriptions of chemical investigations have been very wisely illustrated as much as possible by structural formulas, which will make it easier for most readers to understand the reactions involved. The author has taken it upon himself to suggest structural formulas for certain compounds upon which the chemical investigation is not complete, but he wisely points out that his suggestions have to be taken with certain reservations.

The style is clear and readable and the arrangement of the text material logical and scientifically accurate. The book no doubt will be welcomed by those who are actually engaged in this field of research, for it gives them a convenient source of any desired reference. It constitutes interesting and fascinating reading to those chemists who have not followed carefully the publications regarding the important new developments in the field of sterol chemistry, and for this reason should prove a useful and reliable aid to teachers of general college courses in science.

HANS JENSEN

THE JOHNS HOPKINS UNIVERSITY
SCHOOL OF MEDICINE
BALTIMORE, MARYLAND

INORGANIC CHEMISTRY. *Niels Bjerrum*. Translated from the Third Danish Edition (1932) and brought up to date and adapted to English conditions in collaboration with the author by *R. P. Bell*, M.A., B.Sc., Fellow of Balliol College, Oxford; with a foreword by *F. G. Donnan*, D.Sc., F.R.S., Professor of Chemistry in the University of London. William Heinemann Ltd., London, 1936. American agents, Chemical Publishing Co. of N. Y., Inc., New York City. vi + 317 pp. 17 figs. 14 × 22 cm. $3.50.

The content of this book is divided as follows: Introduction; Atomic Theory; The Non-Metals; The Light Metals; and The Heavy Metals. These main subjects are subdivided into 65 sections. For example, under the Introduction we find five sections, namely, The Concept of Elements; The Most Important Elements; Development of the Concept of Elements; Acids, Salts and Bases; Neutralisation. Under Atomic Theory there are fourteen sections, which are as follows: The Concept of Atoms; Composite Substances; The Concept of Molecules; The Composition of Solutions; The Composition of Chemical Compounds; The Mechanical Theory of Heat; Avogadro's Hypothesis; Determination of the Molecular Weights of Gases; Determination of Atomic Weights; Determination of the Molecular Weight of Dissolved Substances; The Chemical Formulae of a Number of Important Chemical Compounds; Valency; Chemical Calculations; The History of the Atomic Theory.

Hydrogen is the first non-metal to be treated, followed by the halogens, the sulfur group (oxygen and sulfur), the nitrogen group (nitrogen, phosphorus, and arsenic), etc.

Section 25 (about 5 pages) is devoted to the velocity of chemical reactions. A relatively large amount of space (pp. 88–130) is given to the ionic theory, acids and bases, and ionic equations. Chemical equilibrium is discussed in connection with the chemistry of nitrogen, thermochemistry along with carbon, and the colloidal state is introduced after the chemistry of silicon. Radioactivity is taken up in connection with the calcium group; while the periodic system, the structure of atoms, and the electrochemical series are postponed until after the study of aluminum (pp. 246–59). Electrovalency is presented along with the silver group, and oxidizing and reducing agents are discussed in the last section of the book.

Inorganic Chemistry is a scholarly production, and the translator has done his part extremely well. This textbook is a good introduction to *modern* chemical science. Professor Donnan, who wrote the foreword, says: "Although the book is essentially a textbook of inorganic chemistry (as the title implies), there is no fundamental aspect of the vast science of chemistry as it exists today that is not explained and illustrated in a clear and logical manner." He also adds: "A highly important and novel feature of the book is its treatment of the modern generalised

theory of ionisation and reaction in solution, a fundamental advance in chemical science that owes its origin and development to the work of the Danish school of physical chemistry."

It should be added that *Inorganic Chemistry* is conservative in that it contains a vast number of old-fashioned molecular equations, which are still of primary importance in teaching chemistry. One finds, also, many ionic equations, but few electronic equations.

Owing to the small size of the book, it was necessary to omit much of the subject matter ordinarily contained in textbooks of inorganic chemistry. More illustrations would be very helpful; greater space could be devoted with profit to minerals and metallurgy; and the addition of problems and questions would be of assistance to the student. If chosen as a textbook I should agree with Professor Donnan that "it should be used with some book that deals with the historical developments of chemical facts and concepts."

WILLIAM FOSTER

PRINCETON UNIVERSITY
PRINCETON, N. J.

ORGANIC SYNTHESES, VOLUME XVI. *John R. Johnson*, Editor-in-chief. John Wiley & Sons, Inc., New York City, 1936. v + 104 pp. 3 figs. 15 × 23 cm. $1.75.

The current volume of this "Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals" contains directions for the preparation of: β-alanine, 4-aminoveratrole, *n*-butyl nitrite, *n*-butyl phosphate, coupling product of *o*-tolidine and Chicago acid, *sym.*-dimethylhydrazine dihydrochloride, *unsym.*-dimethylhydrazine hydrochloride, 2,5-dimethylpyrrole, 1,4-diphenylbutadiene, epichlorohydrin and epibromohydrin, ethyl phenylmalonate, ethyl *n*-tridecylate, *n*-heptoic acid, *n*-hexaldehyde, isonitrosopropiophenone, methyl benzyl ketone, methylhydrazine sulfate, *p*-nitrobenzyl bromide, 4-nitrophthalic acid, 4-nitrolphthalimide, pelargonic acid, phenanthrene-2- and -3-sulfonates, phthalaldehyde acid, phthalide, quinone, succinimide, tetrahydrofurane, *sym.*-trithiane. An appendix containing later references to preparations in preceding volumes, additions, and corrections for preceding volumes, followed by a subject index, completes the volume.

The utility of this annual is so well appreciated that no further comment is necessary than to say that the present volume is a worthy addition to a series which is indispensable to the organic chemist.

NATHAN L. DRAKE

UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND

THE STRUCTURE OF METALS AND ALLOYS. *William Hume-Rothery*, M.A., D.Sc., Royal Society Warren Research Fellow, Oxford University. Institute of Metals Monograph and Report Series, No. 1. The Institute of Metals, 36 Victoria St., London, S.W. 1, 1936. viii + 112 pp. 61 figs. 14 × 21 cm. 3s. 6d., net.

Resulting largely from the extensive application of X-ray methods to studies of metal and alloy structures during the past fifteen years there has been in this period an extraordinary increase in knowledge and understanding of the relationships between the empirical compositions, structures, and properties of such systems, quite comparable to the revolutionary developments in silicate chemistry during this same time interval. To make these new developments in metal chemistry more available to those not working directly in this field, the Institute of Metals (of Great Britain) asked Dr. Hume-Rothery to write this small book. In the reviewer's opinion they could not have picked a more competent man for the job. The author has been in the forefront of the work in this field during this period and is indisputably an authority on the subject. Moreover he has done an admirable job in presenting the essentials clearly and briefly, yet comprehensively.

Part I is an excellent 14-page introduction to present conceptions of atomic, molecular, and crystal structures. Part II (9 pages) summarizes briefly the crystal structures of the elements, and Part III (20 pages) deals with atomic radii. This much of the book can be considered as merely introductory to the main subject. The reviewer recommends it not only to those interested in metal and alloy structures but also to those others who want a brief, understandable, authoritative presentation of the subjects dealt with. The remainder of the work, dealing with "Primary Metallic Solid Solutions," "Intermediate Phases in Alloy Systems," and "Imperfections in Crystals and Deviations from the Ideal Lattice," is more technical, yet written clearly in non-technical language and emphasizing throughout the principles involved rather than empirical details.

The reviewer offers but two unfavorable criticisms—both minor ones. Although pointing out that Goldschmidt's use of metallic radii for structures containing covalent bonds is not without objection (pp. 35–6) the author makes no mention of the development and use of satisfactory sets of atomic radii (by the reviewer) for just these cases. He also seems unaware of the reviewer's work in 1921 and 1922 relating the crystal structures of the electronegative elements to their atomic structures, giving credit (pp. 24 and 97) for this development to others.

The book is adequately illustrated by simple, well-chosen, and well-reproduced figures. There are few typographical or other errors.

MAURICE L. HUGGINS

THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND

GENERAL COLLEGE CHEMISTRY FOR THE LABORATORY. *Rufus D. Reed*, Associate Professor of Chemistry, and *Robert W. McLachlan*. Assistant Professor of Science, New Jersey State Teachers College. Syllabus form. Lithoprinted, Edwards Brothers, Inc., Ann Arbor, Michigan, 1935. x + 87 pp., one side. 11 figs. 21 × 27.5 cm. $1.80.

The purpose of the book "is an attempt to secure a high degree of correlation of laboratory, classroom, and library work in general college chemistry."

Twenty-three experiments covering the conventional subjects of general chemistry, followed by an introduction to qualitative analysis, make up the content of the book. In the qualitative analysis section, preliminary work on all five groups is treated first. This is followed by the analysis of unknowns in the five groups. No anions are treated.

In stressing the library work the authors cite 140 different reference books. Each experiment is introduced with approximately 30 different references. Thirty to forty questions are incorporated in the directions of each experiment. Following many of the questions, the authors cite references in which additional information about the exercise may be found. Supplementary exercises follow most of the experiments.

If the students have the time to read the references associated with each experiment, the authors will have accomplished the purpose of their book. Most of the references cited in connection with each experiment so overlap and duplicate information as to make one question the number and choice of the references. The most valuable notes are those taken at the time the experiment is performed. If, before writing up his laboratory notes, it were necessary for the student to consult the references following the exercise, there would be some danger that the student might color his observations in the light of the references. The amount of work required in connection with most of the experiments appears to be too much for the conventional freshman laboratory period. It would have been enlightening if the authors had given more information on the practical results obtained from this treatment and the mechanics of its application.

In general the book is well written, with few errors, and the directions are clear. The questions in the experiments are challenging and appropriately placed in the body of the experiments.

C. S. ADAMS

ANTIOCH COLLEGE
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THE BETZ INDICATOR, published monthly by *W. H. & L. D. Betz, Chemical Engineers and Consultants on All Water Problems, 235 W. Wyoming Ave., Philadelphia.* Four-page leaflet, 15 × 22.5 cm. Editorials and questions and answers on water treatment.

THWING'S pH NEWS, issued by *Thwing-Albert Instrument Co., 3339 Lancaster Ave., Philadelphia.* Single-sheet, 20.5 × 27.0 cm. Brief articles on pH control in various industrial processes—*e. g.* (Vol. 1, No. 7), "The importance of pH in the manufacture of clay products."

PROCESS NEWS, issued by *The F. J. Stokes Machine Co., Philadelphia.* Eight-page, 21.5 × 27.5 cm., illustrated. Brief items on "new machines, new methods, new economies."

MONSANTO CURRENT EVENTS, published by and for employees of *Monsanto Chemical Co., St. Louis.* 28-page, 21.5 × 27.5 cm., illustrated. Articles on a wide variety of subjects related to chemical industry; news of Monsanto subsidiaries, products, and employees; humor.

THE ALLOY POT, issued by the *New Jersey Zinc Co., 160 Front St., New York City.* Eight-page, 21.5 × 27.5 cm., illustrated. Brief items dealing, for the most part, with articles die-cast from zinc alloys.

INCO, published quarterly by *The International Nickel Co., 67 Wall Street, New York City.* Current number 36 pp., 22 × 30 cm., illustrated. Articles on nickel and nickel alloys and their uses.

WACO CATALYST, house organ of the *Wilkens-Anderson Co., 111 North Canal St., Chicago.* Brief articles describing various useful pieces of laboratory and demonstration apparatus.

CENCO NEWS CHATS, published monthly by the *Central Scientific Company, 1700 Irving Park Blvd., Chicago.* Descriptions of laboratory apparatus and discussions of applications.

Occasional Trade Literature

LENSES, PRISMS, AND MIRRORS. *Bausch & Lomb Optical Co., Rochester, N. Y.* 20 pp., 21.5 × 28 cm., illustrated. Complete descriptive price list of lenses, prisms, mirrors, quartz optical parts, and miscellaneous optical parts regularly furnished from stock. The company also invites special orders for optical parts to be made up to specifications.

MICROMAX ELECTRICAL CONTROL FOR PROPORTIONING INPUT TO DEMAND. Catalog N-00A. *Leeds & Northrup Co., 4902 Stenton Avenue, Philadelphia.* 8 pp., 19.5 × 26.5 cm., illustrated.

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DAXAD, THE TRUE DISPERSING AGENT. *Dewey and Almy Chemical Company, Cambridge B, Massachusetts.* 8 pp., 21.5 × 28.0 cm., illustrated.

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SCIENTIFIC REFRIGERATION IN RELATION TO NUTRITION AND HEALTH. LULU G. GRAVES. *The Temperature Research Foundation of Kelvinator Corporation, 420 Lexington Ave., New York.* This brochure is one in a series of publications which the Temperature Research Foundation of Kelvinator Corporation plans to issue on various phases of temperature control as it relates to health and leisure.

"An Economist's Appraisal of Domestic Electric Refrigeration," by Dr. Warren M. Persons, former professor of economics at Harvard University and member of The Foundation's Advisory Committee, has already been published.

Others, including scientific reports on progress in refrigeration, air conditioning, and heating, together with a series of home economics manuals, will appear shortly. These publications may be obtained without charge.

New B & L Slide Cooling Attachment

A slide cooling device is essential when projecting photographic color plates and desirable when using expensive hand-colored slides. *Bausch & Lomb* offers an efficient slide cooler in the form of an attachment which holds the temperature down to a safe level. It fits the Models B, BDT or CL Balopticons, and can be used equally well with older Balopticons of these general types.

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Glyco Moves

The Glyco Products Co., Inc., announce that on and after April 25th, their new address is *148 Lafayette St. (near Canal St.), New York.* This move has been made in order to consolidate the laboratories, warehouse, and executive offices. By putting these three branches under one roof, centrally located in lower New York, near the Holland Tunnel, faster and more efficient service and shipments are made possible.

Glycerin in Cooking

The fact that glycerin has an important function in the food industries of the world, both in processing many commercial products and as an adjunct in home cookery, has been known in a generalized way for many years. But work is now in progress which will translate that fact into more specific practical terms, such as actual recipes in which glycerin is used.

Miss Helen Gwetholyn Rees, an independent food consultant who conducts a test kitchen at the Westinghouse Auditorium, at Jamaica, L. I., has just announced to food writers of the country her successful initial results in utilizing the special qualities of glycerin in cooking for the average housewife. In her efforts she also has the coöperation of the Glycerine Producers' Association.

One of the first tested recipes involving glycerin is for a Honey Fruit Tea Bread. It calls for one-quarter of a teaspoon of glycerin for an average small-family baking of this cake. The fruit ingredients—sliced dates, dried apricots, etc.—are rubbed with the glycerin and allowed to stand for half an hour. This, it is reported, not only gives the fruit a brighter appearance but keeps the cake fresh for a much longer period.